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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

New Dodecane. Maurice Delacre (*Bull. Soc. chim.*, 1911, [iv], 9, 1023—1024).—Crude $\gamma\gamma$-dimethyl-Δ^{a}-butylene, $CMe_3\cdot CH:CH_2$ (Abstr., 1906, i, 476), furnishes with hydrogen bromide the compound $CMe_3\cdot CH_2\cdot CH_2Br$ (*loc. cit.*), and this on treatment with sodium yields, in addition to the products described already (*loc. cit.*), the *dodecane* [*$\beta\beta\eta\eta$-tetramethyloctane*], $CMe_3\cdot[CH_2]_4\cdot CMe_3$, b. p. 185—190°, which crystallises in needles and melts at the temperature of the hand to a colourless liquid, possessing a faintly aromatic odour.

T. A. H.

Very Sensitive New Colour Reaction for Ethylenic Linkings and for Tautomeric Modifications. Iwan Ostromisslensky (*J. pr. Chem.*, 1911, [ii], 84, 489—495).—Tetranitromethane dissolved in petroleum (or other paraffin hydrocarbon) produces intense colorations with substances containing ethylenic linkings. The test is responded to by unsaturated hydrocarbons, alcohols, ketones, ethers, esters, and aromatic substances, but not by aromatic nitro-compounds or by many unsaturated carboxylic acids.

The view is generally accepted that a tautomeric substance exists in one definite form in the solid phase, but acquires, in the liquid or gaseous phase, a state of equilibrium between two (or more) modifications, determined by external conditions. This view is substantiated by experiments with tetranitromethane. In aqueous, alcoholic, or ethereal solution, phloroglucinol and ethyl acetoacetate develop

respectively a brownish-red and a golden-yellow coloration. The enolic form of ethyl benzylidenebisacetoacetate, in the solid state or in solution, instantly develops a citron-yellow coloration, whilst the ketonic form remains colourless under similar conditions, although its sodium derivative produces an intense yellow coloration.

Tetranitromethane acts as a mild oxidising agent. It converts quinol into quinhydrone (nitric oxide, nitrous and nitric acids, but not nitroform, have been detected among the products of the reaction), and dimethylaniline into crystal-violet. C. S.

Chemistry of Amyl Compounds. ARTHUR MICHAEL and FRITZ ZEIDLER (*Annalen*, 1911, **385**, 227—292).—The structural theory based on a purely mechanical conception of valency does not suffice to explain many organic reactions, in particular, that of substitution. Many facts are known which show that, for example, the conversion of an alcohol into an alkyl halide by an acid is not merely the substitution of the halogen atom for a hydroxyl group, but must be due to an elimination of water from the alcohol followed by the addition of hydrogen halide to the olefine thus produced. It has been commonly accepted that the elimination of water from the alcohol is due to the dehydrating action of the hydrogen halide. The authors show, however, that in the series of *iso*amyl alcohols the production of an amylene can be effected at 100° by $4{\cdot}5N$-dichloroacetic acid or by $N/50$-hydrochloric acid, although not by water alone; they regard the action of an acid in causing an elimination of water from an alcohol as being due to catalysis, the rate of formation of amylene being faster the more concentrated the acid. This being so, with the necessary consequence that the formation of abnormal substitution products must be conditioned by the molecular structure of the alcohol, the two following problems require solution: (1) which of the several isomerides that could be formed from a given substance in a reaction is actually produced; (2) which of two isomerides that can be converted into the same unsaturated substance is the more easily decomposed. The law of entropy, the "law of addition and elimination," and the thermochemical structure law (Abstr., 1906, i, 550; 1909, i, 494) are applied in answering these questions. The application of these laws leads to the expectations that (1) β-methyl-Δ^{β}-butylene, not β-methyl-Δ^{a}-butylene, will be formed by the dehydration of β-methylbutane-β-ol; (2) β-methylbutane-γ-ol will yield β-methyl-Δ^{β}-butylene almost exclusively: (3) the elimination of water from β-methylbutane-δ-ol will be more difficult than from β-methylbutane-γ-ol, and from β-methylbutane-α-ol more easy than from β-methylbutane-δ-ol; (4) by the action of hydrobromic acid, β-methylbutane-β-ol will yield only the tertiary bromide, β-methylbutane-γ-ol mainly the tertiary bromide, β-methylbutane-δ-ol only the primary bromide, and β-methylbutane-α-ol the primary bromide, together with a little of the tertiary bromide. The experimental results show that these expectations are fulfilled completely in practice. The ease with which the preceding primary, secondary, and tertiary *iso*amyl alcohols yield amylenes varies so much that the authors have based on this property

a method for the detection of each of these alcohols in mixtures of all of them.

The remainder of the paper is mainly an extension of Michael and Leupold's work on the intramolecular transformations of alkyl bromides (Abstr., 1911, i, 250) to the *iso*amyl bromides. C. S.

Metallic Alkyloxides. E. CHABLAY (*Compt. rend.*, 1911, **153**, 953—955. Compare Abstr., 1911, i, 939).—Further experimental details are given for the preparation of metallic alkyloxides according to the methods outlined in an earlier communication. Calcium methoxide, ethoxide, iso*butyloxide*, and iso*amyloxide* have thus been obtained. *Barium methoxide* is particularly easy to prepare by the interaction of sodium methoxide and barium nitrate in liquid ammonia solution. It crystallises in slender needles. *Barium ethoxide* and *strontium methoxide* and *ethoxide* have also been prepared. *Lead methoxide, ethoxide,* iso*butyloxide,* and iso*amyloxide* were obtained by the action of the sodium alkyloxide on lead iodide or nitrate dissolved in liquid ammonia; they are exceeding sensitive to the action of heat or of moisture. W. O. W.

The Action of Certain Acid Chlorides on Potassium Nitrate and the Formation of Acid Anhydrides. OTTO DIELS and HARUKICHI OKADA (*Ber.*, 1911, **44**, 3333—3336).—The authors have investigated the action of acetyl chloride, chloroacetyl chloride, and benzoyl chloride on potassium nitrate, whereby they have obtained good yields of acetic anhydride, chloroacetic anhydride, and benzoic anhydride respectively. They consider that a mixed anhydride is first formed, which subsequently reacts with the excess of acid chloride to form the acid anhydride. This is supported by the fact that acetic anhydride is obtained in 93% yield by the action of acetyl chloride on acetyl nitrate. H. W.

The Photochemical Transformations of Solutions of Ferric Trichloroacetate. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 342—356).—On exposure to light a concentrated (32—33% by weight) solution of ferric trichloroacetate is decomposed, carbon dioxide being evolved and hexachloroethane deposited as a heavy, white precipitate. A dilute solution, owing to hydrolysis, is orange-yellow in colour, and is not sensitive to light; it becomes sensitive, however, if it is rendered colourless by the addition of an excess of trichloroacetic acid. No reaction takes place in the dark.

In the presence of free oxygen, the separation of hexachloroethane may be prevented (in all cases it is diminished) by another reaction, which gives rise to chlorine, hydrogen chloride, and, in the absence of excess of free acid, ferric oxide; a little chloroform is also produced. Trichloroacetic acid acts as an oxygen carrier, the free acid itself being oxidised with liberation of chlorine.

The photochemical reaction takes place in blue light, less rapidly in green light, and not at all in red or yellow light. The light obtained from uviol lamps is convenient to use for the reaction. Rise in temperature first increases the hydrolysis of a solution, and then causes

the liberation of carbon dioxide; at the same time, deposition of ferric oxide takes place and some chloroform is formed. Similarly, thallous tribromoacetate and ferric tribromoacetate both give carbon dioxide and bromoform.

When a $0·68N$-solution of trichloroacetic acid is electrolysed between platinum electrodes, hydrogen is, at first, evolved continuously at the cathode, whereas a discontinuous evolution of gas occurs at the anode. After a time an oily drop forms at the surface of the liquid above the anode, finally becoming of such a size that it breaks away from the liquid surface and falls to the bottom of the solution. The evolution of hydrogen ceases after a time. The electrolyte finally contains carbonyl chloride, chlorine, and hydrochloric acid; the oil formed was trichloromethyl trichloroacetate (compare Kaufler and Herzog, Abstr., 1909, i, 870); it generally solidified at 22°, and the solid had m. p. 32—34°. The presence of carbonyl chloride, etc., in the electrolyte was probably due to the decomposition of this ester by water, according to the equation: $CCl_3·CO_2·CCl_3 + H_2O = CCl_3·CO_2H + HCl + COCl_2$.

The author confirms the results of Anschütz and Emery (Abstr., 1893, i, 188) that trichloromethyl trichloroacetate is a different substance from pentachloroethyl chloroformate, $Cl·CO_2·C_2Cl_5$.

Solutions of ferric pentachloropropionate are very sensitive to light, carbon dioxide being evolved and tetrachloroethylene formed, probably according to the equation:

$$Fe(CO_2·C_2Cl_5)_3 \longrightarrow CO_2 + C_2Cl_4 + Fe(CO_2·C_2Cl_5)_2Cl.$$

The formation of hexachloroethane in the photochemical decomposition of ferric trichloroacetate is possibly due to the decomposition of the anion, thus: $2CCl_3·CO·O' \longrightarrow 2CO_2 + C_2Cl_6$. T. S. P.

Action of Acid Chlorides on Ethyl Diethoxyacetate. Bruno Mylo (*Ber.*, 1911, **44**, 3211—3215).—By the action of phosphorus pentachloride on ethyl diethoxyacetate, *ethyl chloroethoxyacetate*, $OEt·CHCl·CO_2Et$, is formed; it has b. p. 79°/12 mm. On heating with copper powder, it is converted into ethyl $\alpha\beta$-diethoxysuccinate, $C_2H_2(OEt)_2(CO_2Et)_2$, b. p. 140—143°/12·5 mm. In the above reaction phosphorus pentachloride may be replaced by thionyl chloride, acetyl bromide or chloride. Ethyl diethoxyacetate and acetyl bromide give rise to *ethyl ethoxybromoacetate*, b. p. 90—91·5°/11 mm. When acetyl chloride is used, a little copper bronze is required as a catalyst. Benzoyl chloride reacts with the acetal in presence of zinc chloride, but the reaction is obscured by secondary changes. E. F. A.

The Optically Active Dibromosuccinic Acid. Bror Holmberg (*Svensk Kem. Tidskr.*, No. 5, 1911, Reprint, 5 pp. Compare Abstr., 1911, i, 767.)—The author has shown that r-$\alpha\beta$-dibromosuccinic acid is obtained by addition of bromine to maleic acid or maleic anhydride, whilst *meso*-$\alpha\beta$-dibromosuccinic acid is formed by direct bromination of succinic acid or by addition of bromine to fumaric acid.

r-$\alpha\beta$-Dibromosuccinic acid was resolved by means of cinchonine. A crystalline salt, $2C_{19}H_{22}ON_2,C_4H_2O_4Br_2,6H_2O$, separates when aqueous solutions of cinchonine nitrate and sodium $\alpha\beta$-dibromosuccinate are mixed. From this salt, l-$\alpha\beta$-dibromosuccinic acid m. p.

152—154° (decomp.), was isolated. In ethyl acetate it has $[\alpha]_D^{22} - 101 \cdot 4°$, which remained unchanged during two days. In ether it has $[\alpha]_D^{22} - 105 \cdot 4°$; in water, $[\alpha]_D^{24} - 48 \cdot 3°$. After nine days this value had decreased to $[\alpha]_D^{21} - 20 \cdot 15°$. Further purification was effected by dissolving this acid in a mixture of ethyl acetate and carbon tetrachloride. After removal of a crop of less active acid, the filtrate, on evaporation, left a residue of *l*-acid, m. p. 152—153°, which had $[\alpha]_D^{25} - 137 \cdot 6°$ in ethyl acetate. This was the most highly active acid obtained by the author.

Impure *d*-$\alpha\beta$-dibromosuccinic acid was obtained from the filtrate from the original *cinchonine* salt. The crude acid had $[\alpha]_D^{23} + 84 \cdot 9°$ in ethyl acetate. When purified in the manner adopted for the *l*-acid, it had m. p. 151—153°, and $[\alpha]_D^{24} + 126 \cdot 3°$ in ethyl acetate.

Attempts to resolve *r*-$\alpha\beta$-dibromosuccinic acid by means of quinine were less successful.

meso-Dibromosuccinic acid could not be resolved by means of morphine or brucine. H. W.

Preparation of Esters of Orthotrithioformic Acid. JOSEF HOUBEN and KARL M. L. SCHULTZE (*Ber.*, 1911, 44, 3235—3241).—Esters of thiolformic acid should be formed by direct formylation of the mercaptans, according to the equation:

$$R \cdot SH + H \cdot CO_2H = H \cdot CO \cdot SR + H_2O.$$

Owing probably to the fact that the ester produced contains the aldehyde group, the reaction proceeds further, with the formation of esters of orthotrithioformic acid:

$$R \cdot S \cdot CHO + 2R \cdot SH = R \cdot S \cdot CH(SR)_2 + H_2O.$$

The reaction is readily carried out by heating the mercaptan with anhydrous formic acid under reflux for some time; in the case of methyl mercaptan, the reaction mixture is kept in a sealed tube for forty-eight hours at the ordinary temperature.

Methyl orthotrithioformate, $CH(SMe)_3$, is a colourless oil, b. p. 96°/9 mm., 220°/760 mm. (decomp.), which becomes yellow on warming; it solidifies at 16°. The odour is characteristic, but by no means disagreeable. The solution in chloroform decolorises bromine at first, but further addition of bromine leads to the evolution of hydrogen bromide and the formation of a brownish-red coloration, which is not due to bromine. Ethyl orthotrithioformate has b. p. 124—125°/11 mm., 235°/760 mm. (decomp.); the odour is only slight, the ester being purer than that prepared by Holmberg (Abstr., 1907, i, 474). Benzyl orthotrithioformate has m. p. 102·5°. It can be prepared by using oxalic acid in place of formic acid, carbon dioxide being first evolved. p-*Tolyl orthotrithioformate*, $HC(S \cdot C_6H_4Me)_3$, forms snow-white crystals, m. p. 109°. α-*Naphthyl orthotrithioformate*, $HC(S \cdot C_{10}H_{17})_3$, has m. p. 134°. On exposure to light, it gradually becomes pale green in colour. Allyl orthotrithioformate could not be obtained pure.

T. S. P.

Carbithionic Acids. V. Preparation of New Esters of Carbithionic Acid and of Ethyl Chlorocarbithionate. JOSEF HOUBEN and KARL M. L. SCHULTZE (*Ber.*, 1911, 44, 3226—3234).—The ethyl esters of the carbithionic acids are readily obtained by the

action of ethyl sulphate on aqueous solutions of the acids prepared by the action of carbon disulphide on the organo-magnesium compounds (compare Abstr., 1906, i, 847; 1907, i, 382, 474). The method of preparation is similar to that described for the methyl esters, but the esterification with ethyl sulphate does not take place so readily as with methyl sulphate, it being necessary to warm for some time on the water-bath. Moreover, excess of ethyl sulphate does not produce decomposition to the same extent as methyl sulphate, so that in the treatment of the reaction mixture it is not usually necessary to decompose the excess of ethyl sulphate with steam. The yields obtained are generally small, except in the case of α-naphthylcarbithionic esters, where they amount to 40—43%.

Ethyl methylcarbithionate (*ethyl dithioacetate*), $CH_3 \cdot CS_2Et$, is an intense yellow liquid, possessing an odour somewhat similar to that of ethyl acetate. It has b. p. 42—43°/11 mm., D_4^{16} 1·036, and is rapidly oxidised by the air or oxidising agents. With mineral acids or aqueous-alcoholic sodium hydroxide, it gives acetic acid and mercaptan.

Ethyl ethylcarbithionate (*ethyl dithiopropionate*), $C_2H_5 \cdot CS_2Et$, has b. p. 60—61°/10 mm. It is a yellow liquid with a pronounced, characteristic odour. Methyl phenylcarbithionate (methyl dithiobenzoate), $C_6H_5 \cdot CS_2Me$, was obtained in a slightly purer condition than the specimen prepared by Höhn and Bloch (Abstr., 1910, i, 256), and had b. p. 141—142°/12 mm. At the temperature of liquid air it forms a flesh-coloured, solid mass. *Methyl α-naphthylcarbithionate* (*methyl dithio-α-naphthoate*), $C_{10}H_7 \cdot CS_2Me$, forms orange-yellow needles, which melt to a dark red oil at 54°, b. p. 210°/15 mm. It is quite stable in the air, as also is *ethyl α-naphthylcarbithionate* (*ethyl dithio-α-naphthoate*), $C_{10}H_7 \cdot CS_2Et$, which forms orange-yellow crystals, melting to a dark red oil at 39—40°. Both these esters are stable towards dilute and concentrated hydrochloric acid, but are decomposed in the usual way by aqueous-alcoholic sodium hydroxide.

Ethyl chlorocarbithionate (ethyl chlorodithioformate), $Cl \cdot CS_2Et$, is obtained by the gradual addition (lasting twenty-four hours) of thiocarbonyl chloride (25 grams) to a solution of ethyl mercaptan (13·5 grams) in carbon disulphide (75 c.c.), and fractionation of the reaction mixture, after further keeping for two days, under diminished pressure. It forms an intense reddish-yellow oil, which excites to tears and has a penetrating odour, b. p. 80—81°/19 mm. and 74—75°/15 mm. It is stable when kept away from air and moisture. It reacts with amino-acids; for example, on shaking with an aqueous solution of potassium anthranilate, a red oil is formed, which rapidly crystallises, and is probably $CO_2H \cdot C_6H_4 \cdot NH \cdot CS_2Et$. With organo-magnesium compounds, it reacts according to the equation:

$$RMgX + Cl \cdot CS_2Et = R \cdot CS_2Et + ClMgX.$$

With a solution of sodium iodide in acetone, it gives the corresponding iodo-compound. When reduced with potassium arsenite in alkaline solution, a brown oil is obtained, which, on fractional distillation, gives a light yellow oil with b. p. 131—132°/19 mm. and 115°/11 mm. The composition corresponds with that of ethyl thioformate

($H\cdot CS_2Et$), but the high boiling point indicates that it is probably a polymeride of that substance.

In the preparation of ethyl chlorocarbithionate, a by-product, b. p. 115—125°/19 mm., is obtained, especially if the reaction mixture is not too strongly diluted with carbon disulphide, which is probably ethyl trithiocarbonate. T. S. P.

α-Bromoacraldehyde. ROBERT LESPIEAU (*Compt. rend.*, 1911, **153**, 951—953).—Pyrazole is produced when α-bromoacraldehyde is added to a solution of hydrazine hydrate. The aldehyde does not unite with hydrogen cyanide unless a trace of potassium cyanide is present, when the action becomes violent. Hydrolysis of the resulting *nitrile* leads to formation of *β-bromo-α-hydroxy-Δ^{β}-butenoic acid*, $CH_2{:}CBr\cdot CH(OH)\cdot CO_2H$, m. p. 119—120°; the *potassium* salt is very deliquescent; the *ethyl* ester has b. p. 216—217°/750 mm.

ββγ-Tribromo-α-hydroxybutyric acid, $CH_2Br\cdot CBr_2\cdot CH(OH)\cdot CO_2H$, obtained by the action of bromine on the foregoing unsaturated acid, has m. p. 140—141°. The high boiling residue from the distillation of α-bromoacraldehyde yields a nitrile under the above-mentioned conditions. On hydrolysis a mixture of acids is obtained, from which crystals, m. p. 104—105°, have been isolated; they probably consist of *βγγ-tribromo-α-hydroxybutyric acid*, which arises from the presence of βγγ-tribromopropionaldehyde in the original aldehyde.

W. O. W.

Attempt at the Direct Preparation of Tetrolaldehyde. PAUL L. VIGUIER (*Compt. rend.*, 1911, **153**, 955—957).—In the expectation of obtaining tetrolaldehyde, diethylformamide (1 mol.) was treated with the magnesium derivative of bromopropinene (1 mol.). After the usual treatment, the product was found to consist of unaltered amide with *δ-diethylamino-$\Delta^{\beta\epsilon}$-heptadi-inene*,

$$CMe{:}C\cdot CH(NEt_2)\cdot C{:}CMe,$$

an oily liquid, b. p. 99—99·5°/14—15 mm., D_0^{18} 0·871, n_D^{18} 1·477. The *picrate* occurs in slender needles, m. p. 169°; the *platinichloride* crystallises with $2H_2O$, and decomposes at 120°; the *ethiodide* decomposes at 148—150°.

When the magnesium derivative of bromopropinene is treated with excess of ethyl formate, *δ-hydroxy-$\Delta^{\beta\epsilon}$-heptadi-inene*,

$$CMe{:}C\cdot CH(OH)\cdot C{:}CMe,$$

results instead of the expected aldehyde. This substance resembles boric acid in appearance, and has m. p. 105—106°. The required aldehyde appears to be produced when the sodium derivative of propinene is treated with ethyl formate, but the reaction is so slow that decomposition occurs and no definite product can be isolated. W. O. W.

Catalytic Reactions at High Pressures and Temperatures. XXIII. Hydrogenation of Acetone in the Presence of Copper Oxide and Zinc Dust. WLADIMIR IPATIEFF and G. BALATSCHINSKY (*Ber.*, 1911, **44**, 3459—3461).—The action of zinc dust and of copper oxide as catalysts on the hydrogenation of acetone under pressure has

been investigated (compare Abstr., 1907, i, 828). An iron tube was used, the temperature being 280—300°, it having been proved that iron has no catalytic effect at 300°. The initial pressure of the hydrogen was 100—130 atmospheres.

With copper oxide as catalyst the resulting product contains 65% of *iso*propyl alcohol, whilst the percentage when zinc is used is about 50%.

It was also shown that with initial hydrogen pressures of 40 atmospheres, *iso*propyl alcohol gives acetone and hydrogen at 300°, with zinc dust as catalyst. Also, with acetone and copper oxide, condensation products of an unsaturated character are formed. Thus the reaction: $CHMe_2 \cdot OH \rightleftharpoons H_2 + COMe_2$ is reversible in the presence of zinc dust or copper oxide. T. S. P.

The Electrolytic Reduction of Ketones. JULIUS TAFEL [with WILHELM SCHEPSS] (*Zeitsch. Elektrochem.*, 1911, **17**, 972—976. Compare Abstr., 1911, i, 784).—Acetone and methyl ethyl ketone are readily reduced electrolytically to the corresponding saturated hydrocarbons at a cadmium cathode in sulphuric acid solution. With the higher aliphatic ketones, for example, methyl *iso*amyl ketone, similar results can only be obtained with very high current densities (compare Abstr., 1909, i, 766).

Similar results are obtained with mercury and lead cathodes in the case of acetone, but the yield of propane is not so great, owing to side reactions, such as, in the case of lead cathodes, the formation of *iso*propyl alcohol, pinacone, and lead alkyls.

*iso*Propyl alcohol does not undergo reduction under conditions which lead to the formation of propane from acetone. T. S. P.

The Action of Chlorine on Hexonic Acids (Hexonsäuren) [Maltol]. PAUL DREVERHOFF (*Chem. Zeit.*, 1911, **35**, 1323).—The substance (maltol; compare Abstr., 1910, i, 225, 544) which is formed when moist malt, etc., is heated, is decomposed by chlorine, 2 molecules of the substance yielding first salicylic acid and then phenol. Traces of maltol are present in certain dark-coloured beers, and may be detected by adding a very small quantity of chlorine to the beer, an odour of phenol being produced immediately. W. P. S.

Degradation of *iso*Rhodeose. EMIL VOTOČEK and CYRILL KRAUZ (*Ber.*, 1911, **44**, 3287—3290).—The configuration,

$$CHO\cdot\overset{OH}{\underset{H}{C}}—\overset{H}{\underset{OH}{C}}—\overset{OH}{\underset{H}{C}}\cdot CH(OH)\cdot CH_3,$$

previously assigned to *iso*rhodeose (Abstr., 1911, i, 354) has now been confirmed by oxidation of the sugar with bromine to *iso*rhodeonic acid, treatment of the calcium salt of this with hydrogen peroxide and iron, and oxidation of the methyltetrose formed with nitric acid to tartaric acid. The modification formed is shown to be *l*-tartaric acid,

$$CO_2H\cdot\overset{H}{\underset{OH}{C}}—\overset{OH}{\underset{H}{C}}\cdot CO_2H.$$

E. F. A.

Behaviour of Sucrose and its Decomposition Products on Heating. IV. Reducing Substances in the Refinery Products. J. E. Duschsky (*Zeitsch. ver. deut. Zuckerind.*, 1911, 989—1005. Compare Abstr., 1911, i, 769).—In the refinery, sugar solutions are only exposed to a high temperature for a relatively short time, but undergo protracted treatment at lower temperatures. The formation of reducing substances has been followed quantitatively in great detail throughout every stage of the process.

In the melting department there is an increase of reducing substance which is greatest when the crude sugar is dissolved in waste water, and least when dissolution is effected in pure water.

There is a considerable increase of reducing substance in a relatively short time when the syrup is left at a high temperature in the boilers of the melter. The filtration of the syrup through bone charcoal does not cause any increase in the reducing substances. During the boiling of the raffinade syrup there is no noticeable increase in the reducing substances; the same applies to the interval during crystallisation and subsequent drying of the crystals. E. F. A.

Sugar Solutions and Lime. P. J. H. von Ginneken (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 442—461. Compare Claasen, Abstr., 1911, i, 606).—From the point of view of the phase rule the author first gives a theoretical discussion of the phenomena which are likely to be observed in systems containing the three components: lime, sugar, and water. Details are then given of experiments on the decomposition of the trisucrate, and on the position of the eutectic line at 80°. The solubility of calcium hydroxide in sugar solutions of varying concentrations at 80° was also determined.

The results obtained are applied to the explanation of various well-known facts. T. S. P.

Methylethylammonium Chlorides. John E. Mackenzie (*J. pr. Chem.*, 1911, [ii], **84**, 549—554).—For the purpose of a comparative study of their toxic actions, the methylethylammonium chlorides intermediate between tetramethyl- and tetraethyl-ammonium chloride have been prepared by the direct interaction of an amine and an alkyl chloride in alcoholic solution at 40—60°. C. S.

The Behaviour of Certain Hydroxides towards Solutions of Alkylenediamines. Wilhelm Traube (*Ber.*, 1911, **44**, 3319—3324).—Whilst copper hydroxide is only slightly soluble in aqueous solutions of primary aliphatic amines and insoluble in solutions of secondary aliphatic amines, it dissolves readily in aqueous solutions of aliphatic diamines. Whether in concentrated or dilute solution, two molecules of ethylenediamine were found to dissolve one molecule of copper hydroxide. The formula, $[Cu(C_2H_8N_2)_2](OH)_2$, is ascribed to the compound so formed, which could not, however, be obtained in the solid state. The solutions have a deep bluish-violet colour, absorb oxygen from the air, and readily dissolve cellulose.

A similar reaction occurs with propylenediamine and copper hydroxide.

The hydroxides of nickel, cobalt, zinc, and cadmium, and the oxides of silver and mercury are also soluble in solutions of alkylenediamines. The respective formulæ, $[Ni(C_2H_8N_2)_3](OH)_2$, $[Zn(C_2H_8N_2)_6](OH)_2$, and $[Ag(C_2H_8N_2)_3]OH$, have been assigned to the nickel, zinc, and silver complexes.

The solutions were prepared by shaking the metallic hydroxide, or oxide in the case of silver, with aqueous solutions of ethylenediamine. The solutions containing zinc and nickel were found to be more readily obtained by shaking the metal with aqueous ethylenediamine in the presence of oxygen. H. W.

The Asymmetric Cobalt Atom. III. and IV. ALFRED WERNER (*Ber.*, 1911, **44**, 3272—3278, 3279—3284).—III.—The present paper deals with the resolution of 1 : 2-chloronitrodiethylenediaminecobaltic salts, $\left[\begin{smallmatrix}Cl \\ NO_2\end{smallmatrix} Co\ en_2\right]X$, into their optical isomerides. Theoretically, the optical isomerism of these salts is of the same type as that of 1 : 2-chloroamminediethylenediaminecobaltic salts, $\left[\begin{smallmatrix}Cl \\ H_3N\end{smallmatrix} Co\ en_2\right]Cl_2$, dealt with in the first paper of this series (Abstr., 1911, i, 613), except that two acid groups are now in direct combination with the cobalt atom, so that the complex is univalent.

Although the 1 : 2-chloronitrodiethylenediaminecobaltic salts show a great tendency to form aquo-salts in aqueous solution, it was found possible to resolve them by means of the silver camphorsulphonates. The least soluble isomerides are *l*-chloronitrodiethylenediaminecobaltic *d*-camphorsulphonate and *d*-chloronitrodiethylenediaminecobaltic *l*-bromocamphorsulphonate and from these the iodides could be obtained by means of sodium iodide. Owing to the formation of aquo-salts, however, it was difficult to obtain the active isomerides in quantity by this method. Much better results were obtained by a method similar to that used in the resolution of chromium compounds (Abstr., 1911, i, 960). When *d*-ammonium camphorsulphonate or *d*-ammonium bromocamphorsulphonate is added to a freshly prepared, saturated solution of 1 : 2-chloronitrodiethylenediaminecobaltic chloride, crystals of l-*chloronitrodiethylenediaminecobaltic* d-*camphorsulphonate* or of d-*chloronitrodiethylenediaminecobaltic* d-*bromocamphorsulphonate* are deposited in a pure condition after a short time. From these the corresponding chlorides can be obtained by solution in concentrated hydrochloric acid and precipitation with alcohol.

The active chloronitrodiethylenediaminecobaltic salts show the phenomenon of mutarotation. The initial rotation gradually increases, the colour of the solution at the same time changing from red to yellow, owing to the formation of *cis*-nitroaquo-salts, in accordance with the equation: $\left[\begin{smallmatrix}Cl \\ NO_2\end{smallmatrix} Co\ en_2\right]Cl + H_2O = \left[\begin{smallmatrix}H_2O \\ NO_2\end{smallmatrix} Co\ en_2\right]Cl_2$. Also, by interaction with sodium nitrite they can be transformed without loss into the dinitro-salts, and the dinitro-perchlorates so obtained have $[\alpha]_D$ + 39° and − 40° in a 1% solution, which is the

same as that obtained with the active dinitro-salts obtained by direct resolution (Abstr., 1911, i, 838).

d- and l-1 : 2-*Chloronitrodiethylenediaminecobaltic chlorides*,

$$\left[\begin{matrix}Cl\\NO_2\end{matrix}\ Co\ en_2\right]Cl,$$

have $[\alpha]_D$ + 20° and − 21·5° respectively. In 50% (by volume) hydrochloric acid solution they have $[\alpha]_c$ + 16° and − 16·5°, and $[\alpha]_D$ ± 25°; the hydrochloric acid solution is more stable than the aqueous solution. In aqueous solution the rotation gradually increases to $[\alpha]_c$ + 31° and − 35°, $[\alpha]_D$ + 52° and − 48°, owing to the formation of the d- and l-*nitroaquodiethylenediaminecobaltic chlorides*, $\left[\begin{matrix}H_2O\\NO_2\end{matrix}\ Co\ en_2\right]Cl$. From these solutions potassium iodide precipitates a periodide, from which the active iodide can be isolated. After keeping for weeks, the solutions become inactive.

l-1 : 2-*Nitrothiocyanatodiethylenediaminecobaltic chloride*,

$$\left[\begin{matrix}NO_2\\SCN\end{matrix}\ Co\ en_2\right]Cl,$$

is obtained from the chloronitro-salt by interaction with potassium thiocyanate. It has $[\alpha]_c$ − 50°, $[\alpha]_D$ − 84°. l-*Chloronitrodiethylenediaminecobaltic nitrate*, $\left[\begin{matrix}Cl\\NO_2\end{matrix}\ Co\ en_2\right]NO_3$, is prepared from the chloride by interaction with nitric acid. It has $[\alpha]_c$ − 10°, $[\alpha]_D$ − 36·5°.

IV.—The 1 : 2-dichlorodiethylenediaminecobaltic salts, $[Cl_2\ Co\ en_2]X$, are of the same type as the corresponding dinitro-salts (Abstr., 1911, i, 838), and can be resolved into the optical isomerides. Owing to the ready formation of the chloroaquo- and diaquo-salts in aqueous solution, the resolution is best accomplished by means of *d*- and *l*-ammonium bromocamphorsulphonates, the method used being similar to that just described. The least soluble salts are l-*dichlorodiethylenediaminecobaltic* d-*bromocamphorsulphonate* and d-*dichlorodiethylenediaminecobaltic* l-*bromocamphorsulphonate*. From these salts the *chloride*, *bromide*, and *nitrate* are readily obtained by treatment with the appropriate acids. The *sulphate* and *dithionate* are prepared from the chloride by reaction with ammonium sulphate and sodium dithionate, respectively. The optical rotations (for white light) of these salts are as follows:

	[α].	[M].		[α].	[M].
Chloride	+184°	+558°	Sulphate	+180°	+536°
	−200	−607		−182	−540·5
Bromide	+168°	+554°	Dithionate	+160°	+542°
	−176	−581		−164	−556
Nitrate	+164°	+511°			
	−164	−511			

The above values are not very accurate, owing to the fact that the rotations of the aqueous solutions diminish very rapidly, generally becoming zero after about three hours. The solid salts preserve their activity unchanged, so that the racemisation in solution must be referred to the action of the solvent, which forms chloroaquo- and

diaquo-salts. The exact process of racemisation cannot be given as yet. In some cases the chlorine atoms in the complex can be replaced by other acid radicles without loss of activity; for example, with potassium carbonate, an active carbonatodiethylenediaminecobaltic salt is formed, which is readily isolated from some inactive salt produced at the same time; the salt rotates in a direction opposite to that of the dichloro-salt from which it was made. In other cases the replacement of the chlorine atoms in the complex gives inactive salts, for example, inactive 1 : 2-hydroxyaquo- and 1 : 2-dinitro-diethylenediaminecobaltic salts.

Racemic 1 : 2-dichlorodiethylenediaminecobaltic chloride is best prepared as follows: Finely powdered carbonatodiethylenediaminecobaltic chloride is heated on the water-bath with a saturated solution of hydrogen chloride in absolute alcohol until the red colour of the salt changes to violet. The violet salt is collected and digested at the ordinary temperature with successive portions of aqueous alcohol (1 : 1) until the filtrate is no longer coloured green, but violet. The salt is then washed with absolute alcohol and ether.

l - *Dichlorodiethylenediaminecobaltic* d - *bromocamphorsulphonate*, $[Cl_2 Co\ en_2]O_3S{\cdot}C_{10}H_{14}OBr$, forms violet crystals, and has [M] −414°. The corresponding d-l-*salt* has [M] + 381°. Active l-*dichlorodiethylenediaminecobaltic chlorides*, YCl,H_2O, where $Y = [Cl_2 Co\ en_2]$, crystallise in violet-coloured leaflets. The *active bromides*, YBr, form crystals, which are coloured almost indigo-blue. The *active nitrates*, YNO_3, give small, violet crystals; those of the *sulphates*, Y_2SO_4, are coloured dark violet, whilst those of the *dithionates*, $Y_2S_2O_6,H_2O$, are light violet in colour. T. S. P.

Action of Sodium Hypochlorite on Hexamethylenetetramine. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1911, [iv], 9, 1025—1029).—Sodium hypochlorite reacts with aqueous solutions of hexamethylenetetramine to form *N*-dichloropentamethylenetetramine, but in presence of acetic acid gives *N*-trichlorotrimethylenetriamine (1 : 3 : 5-trichlorohexahydrotriazine), which is isomeric with Cross, Bevan, and Bacon's methylenechloroamine (Trans., 1910, 97, 2404).

N-*Dichloropentamethylenetetramine*, $C_5H_{10}N_4Cl_2$, crystallises in brilliant lamellæ from water, or in octahedra from ether, possesses the odour peculiar to compounds containing chlorine and nitrogen, is sparingly soluble in water, and moderately so in ether or benzene, and deflagrates at 78—82°, giving an odour of carbylamines. It can be kept for long periods in sealed tubes, but decomposes in the course of a few days on exposure to air, forming ammonium chloride and hexamethylenetetramine hydrochloride. With sodium hydroxide in alcohol, ammonia is produced, and the chlorine is removed as alkali chloride.

1 : 3 : 5-Trichlorohexahydrotriazine (Abstr., 1899, i, 326),

$$CH_2{<}{\begin{matrix}NCl{-}CH_2\\NCl{-}CH_2\end{matrix}}{>}NCl,$$

crystallises in brilliant needles, has a slight odour of chlorine, is nearly insoluble in water, but soluble in alcohol or chloroform, and deflagrates at 78°, evolving fumes having the odour of hydrogen cyanide and carbylamines, and leaving a residue of ammonium chloride. It decomposes in

air, or when kept in solution in organic solvents. With sodium hydroxide in alcohol, it yields ammonia and sodium chloride, and the residue on distillation with a dilute acid gives formic acid: this decomposition appears to take place in accordance with the equations:

$$(1)\ (CH_2{:}NCl)_3 + 3NaOEt = 3NaCl + 3CH(NH)\cdot OEt;$$
$$(2)\ CH(NH)\cdot OEt + 2H_2O = H\cdot CO_2H + EtOH + NH_3.$$

T. A. H.

Condensation of Amino-acids in Presence of Glycerol: *cyclo*-Glycylglycines and Polypeptides. LOUIS C. MAILLARD (*Compt. rend.*, 1911, **153**, 1078—1080).—Attempts to prepare glycerides of amino-acids have proved unsuccessful. Glycine is converted into diketopiperazine by heating with four or five times its weight of glycerol for some hours. The yield of the pure anhydride is 80%. Other condensation products are also formed under these conditions; triglycylglycine occurs as an intermediate product, but this in turn loses water, forming the anhydride, together with pentaglycylglycine and a brown oxidation product. The yield of polypeptides is greatly increased by employing a smaller proportion of glycerol. By the same method sarcosine and alanine have been transformed into their cyclic anhydrides, and leucine into leucinimide. The reaction appears to be general, and can be applied to the preparation of mixed anhydrides. It probably involves formation of an unstable glyceride, which decomposes, losing glycerol and water. The suggestion is made that the synthetic reactions effected by enzymes are of this type.

The author proposes to use the prefix *cyclo* for the anhydrides of amino-acids; thus diketopiperazine is termed *cyclo*glycylglycine, and the condensation product of tyrosine and leucine becomes *cyclo*-tyrosyl-leucine. W. O. W.

Synthesis of Amino-acids. IX. Racemic Arginine (α-Amino-δ-guanidino-*n*-valeric Acid) and the Isomeric δ-Amino-α-guanidino-*n*-valeric Acid. SÖREN P. L. SÖRENSEN, MARGRETHE HÖYRUP, and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1911, **76**, 44—94. Compare Abstr., 1910, i, 227).—In part already published.

When ornithuric acid is treated with warm concentrated hydrochloric acid, pure δ-monobenzoylornithine,

$$COPh\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

is obtained. On boiling ornithuric acid, however, with $N/5$-barium hydroxide, the product is α-monobenzoylornithine,

$$NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH\cdot COPh)\cdot CO_2H.$$

Under suitable experimental conditions the yield of both these compounds is satisfactory.

When the amino-group is eliminated, α-monobenzoylornithine is converted into δ-hydroxy-α-benzoylamino-*n*-valeric acid,

$$OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH\cdot COPh)\cdot CO_2H,$$

whilst δ-monobenzoylornithine yields α-hydroxy-δ-benzoylamino-*n*-valeric acid. When the benzoyl group is eliminated, the δ-amino-α-hydroxy-*n*-valeric acid described by Fischer and Zemplen (Abstr., 1910, i, 100) is obtained.

From both the isomeric monobenzoylornithines the corresponding guanidinomonobenzoylamino-*n*-valeric acids are obtained on the addition of cyanamide, and these after removal of the benzoyl group are converted into the isomeric aminoguanidino-*n*-valeric acids. That from α-monobenzoylornithine, which must have the formula

$$NH_2\cdot C(:NH)\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

proved to be in every way identical with *racemic* arginine. The isomeric δ-amino-α-guanidino-*n*-valeric acid had entirely different properties, and readily lost water, forming an anhydride.

The yield in each of these operations amounted to 60% or more of the possible, and a rearrangement at any stage is considered impossible. It is also proved that the cyanamide addition takes place at the free primary amino-group and not at the secondary amino-group, since the monobenzoylguanidinovaleric acids cannot be titrated in presence of formaldehyde.

α-Monobenzoylornithine, m. p. 264—267° (Maquenne block), forms long crystals, some rectangular, others flat needles. On treatment with barium nitrite, α-benzoylamino-δ-hydroxy-*n*-valeric acid is obtained.

α-Monobenzoylamino-δ-guanidino-*n*-valeric acid is obtained by the addition of cyanamide to α-monobenzoylornithine dissolved in barium hydroxide; it has m. p. 315°, shows no alteration in acidity on the addition of formaldehyde, and is in every way identical with natural *racemic* monobenzoyl arginine. Synthetic arginine nitrate, arginine copper nitrate, and arginine picrate are in every respect the same as the natural racemic products.

δ-Monobenzoylornithine (Fischer, *Ber.*, 1901, **34**, 463), m. p. 285—288°, crystallises in rhomboidal or six-sided plates; with barium nitrite, *α-hydroxy-δ-benzoylamino*-n-*valeric acid* is obtained, forming a colourless, crystalline mass of bundles of prismatic needles, m. p. 85°.

δ-Monobenzoylamino-α-guanidino-*n*-valeric acid,

$$C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH\cdot C[:NH]\cdot NH_2)\cdot CO_2H,$$

forms a cheese-like precipitate, consisting of lumps of slender needles, m. p. 175°. When boiled with concentrated hydrochloric acid, it does not form α-proline. On heating for three hours at 140—150° with 33% hydrochloric acid, the *hydrochloride* of *δ-amino-α-guanidino*-n-*valeric anhydride*, $NH<\begin{matrix}CO\text{——}CH\cdot[CH_2]_3\cdot NH_2,2HCl \\ C(:NH)\cdot NH\end{matrix}$, is obtained as colourless, prismatic crystals in stellar aggregates, m. p. 200°. The *picrate* forms long, yellow needles, m. p. 240—245°.

Ethyl γ-cyanoaminopropylphthaliminomalonate,

$$C_6H_4:C_2O_2:N\cdot C(CO_2Et)_2\cdot[CH_2]_3\cdot N:C:NH,$$

from ethyl γ-bromopropylphthaliminomalonate and sodium cyanamide, separates in well-formed colourless, short, stout, prismatic crystals, m. p. 191°; it can be titrated as a monobasic acid, using phenolphthalein.

Ethyl γ-cyanoaminopropylphthaliminomalonamide,

$$C_6H_4:C_2O_2:N\cdot C(CO_2Et)(CO\cdot NH_2)\cdot[CH_2]_3\cdot N:C:NH,$$

prepared by the action of concentrated ammonia on the above, crystallises in prismatic needles.

γ-Cyanoaminopropylphthaliminomalonamic acid,

$$C_6H_4{:}C_2O_2{:}N\cdot C(CO_2H)(CO\cdot NH_2)\cdot[CH_2]_3\cdot N{:}C{:}NH,$$

forms long, prismatic, obliquely-cut prisms. It behaves as a dibasic acid.

γ-Cyanoaminopropylphthaliminomalonic acid,

$$C_6H_4{:}C_2O_2{:}N\cdot C(CO_2H)_2\cdot[CH_2]_3\cdot N{:}C{:}NH,$$

crystallises in stellar aggregates of microscopic needles; it is tribasic. On treatment of these compounds with aqueous ammonia, anhydrous ammonia, or ammonium salts, it was not possible under any conditions to obtain guanidino-compounds. E. F. A.

Hypoiodous Amides. ETIENNE BOISMENU (*Compt. rend.*, 1911, **153**, 948—951. Compare Abstr., 1911, i, 957).—Iodoacetamide, $CH_3\cdot CO\cdot NHI$, is obtained as a colourless substance, m. p. 143° (decomp.), by the alternate addition in small quantities of iodine (7 grams) and silver oxide to a solution of acetamide (1·475 grams) in ethyl acetate (100 c.c.), the liquid being finally evaporated to dryness, and the residue washed with chloroform. *Iodopropionamide* occurs in crystals, m. p. 128° (decomp.). *Iodoformamide*, m. p. 95° (decomp.), is less stable than the foregoing, and rapidly decomposes at the ordinary temperature, even in a vacuum. Iodobenzamide could not be obtained in the pure state. The substances described closely resemble the corresponding bromo-derivatives. W. O. W.

The Formation of Symmetrical Dialkylcarbamides by Heating the Corresponding Carbamates. FRITZ FICHTER and BERNHARD BECKER (*Ber.*, 1911, **44**, 3481—3485. Compare this vol., ii, 45).—The alkyl substituted ammonium carbamates when heated under pressure give, like ammonium carbamate, an equilibrium with the corresponding carbamide; the optimum temperature is, however, generally higher and the yield better than in the formation of the unsubstituted carbamide.

Methylammonium methylcarbamate was obtained from dry carbon dioxide and methylamine gas in crystalline crusts which smell strongly of methylamine and have m. p. 105°; it is deliquescent, and its aqueous solution is strongly alkaline, owing to hydrolysis. After heating in a sealed glass tube and subsequent removal of unchanged methylcarbamate, practically pure *s*-dimethylcarbamide (m. p. 96°) remains.

Ethylammonium ethylcarbamate, prepared similarly, is a white, crystalline salt, m. p. 118° (in sealed tube). On heating, it gives diethylcarbamide (m. p. 106°), the optimum temperature being about 150°, the equilibrium mixture at this temperature containing 59—60% of the diethylcarbamide.

Benzylammonium benzylcarbamate, obtained by the action of carbon dioxide on a dry ethereal solution of benzylamine, separated as a gelatinous precipitate, which slowly changed to a crystalline mass, m. p. 100° (compare Tiemann and Friedländer (Abstr., 1882, 56). On heating it yields dibenzylcarbamide.

Benzhydrylammonium benzhydrylcarbamate, formed by the action of carbon dioxide on benzhydrylamine in ethereal solution, is a white

substance which decomposes on warming with water, and has m. p. 165° (with decomp.). On heating, instead of the expected carbamide, there is formed *tribenzhydrylamine*, $N(CHPh_2)_3$; this amine crystallises in needles, m. p. 144°, and forms a *picrate* insoluble in benzene.

Diethylammonium diethylcarbamate was produced by the combination of carbon dioxide with the vapour of diethylamine; it is a white, crystalline mass, melting at room temperature, and turning brown when kept. If carbon dioxide is led into diethylamine in the liquid or dissolved state, the product is *diethylammonium hydrogen carbonate*, which in a sealed tube melts and decomposes at 70°. If the above diethylcarbamate is heated, although the reaction product always possesses the characteristic odour of tetraethylcarbamide, no weighable quantity of this substance is isolable.

Hydrazine hydrazinecarboxylate is exceptional in its behaviour, and on heating under reflux at 140° gives a practically theoretical yield of carbohydrazide (compare Stollé and Hofmann, Abstr., 1905, i, 28); however, *ammonium hydrazinecarboxylate*, an unstable, deliquescent substance obtained by the action of ammonia on hydrazine hydrazinecarboxylate or on hydrazinecarboxylic acid, behaves analogously to the above-mentioned carbamates in being incompletely converted by heat into semicarbazide. D. F. T.

Storage of Calcium Cyanamide in the Tropics. C. J. Milo (*Chem. Zentr.*, 1911, ii, 1655—1656; from *Med. Proefstat. Java-Suikerind.*, 1911, 3, 311—363).—When a concentrated aqueous extract of calcium cyanamide is kept for some days, a crystalline, basic calcium salt, $C(N\cdot CaOH)_2$, is obtained. The same salt is produced, along with cyanamide, dicyanamide, and carbamide when calcium cyanamide is kept for a long time in warm, damp air. N. H. J. M.

Interaction of Thiocyanates and Bromine in Aqueous Solution. W. König (*J. pr. Chem.*, 1911, [ii], 84, 558—560).—2*N*-Bromine in 10% potassium bromide reacts quantitatively with aqueous potassium or ammonium thiocyanate in accordance with the equation: $KSCN + 4Br_2 + 4H_2O = KBr + CNBr + H_2SO_4 + 6HBr$; so also does chlorine, but not iodine. The strengths of aqueous bromine or thiocyanate solutions, therefore, can be determined by titration with standard potassium hydroxide. C. S.

Constitution of Aliphatic Diazo-compounds and of Azoimide. Johannes Thiele (*Ber.*, 1911, 44, 3336. Compare Abstr., 1911, i, 845).—The author acknowledges that Angeli has previously proposed a formula, which contains the group C:N:N, for a diazo-compound of indole; also that he has put forward the formulæ $N⋮N:CH_2$ and $N⋮N:NH$ for diazomethane and azoimide respectively.

H. W.

1 : 2-Dimethyl*cyclo*propane. Nicolai D. Zelinsky and M. N. Ujedinoff (*J. pr. Chem.*, 1911, [ii], 84, 543—548).—α-Acetyl*iso*propyl alcohol (hydracetylacetone), for the preparation of which an improved method is described, is reduced by sodium amalgam and water in an atmosphere of carbon dioxide to *pentane-βδ-diol*,

$$OH\cdot CHMe\cdot CH_2\cdot CHMe\cdot OH,$$

b. p. 197·5—198·5°/750 mm. or 97—98°/13 mm., D_4^{20} 0·9635, n_D^{20} 1·4349, which is converted by phosphorus tribromide at 100°, and finally at 140°, into βδ-dibromopentane, b. p. 60°/12 mm., D_4^{20} 1·6659, and n_D^{20} 1·4987. By reduction with zinc dust and 80% alcohol in a freezing mixture, the dibromide yields 1 : 2-*dimethyl*cyclo*propane*, b. p. 32—33°, D_4^0 0·7025, D_4^{20} 0·6806, n_D^{20} 1·3763, n_D^{10} 1·3823, which is oxidised by 1% potassium permanganate, and, in contrast to 1 : 1-dimethyl*cyclo*propane, reacts slowly with bromine and is sparingly soluble in diluted sulphuric acid (2 vols. of acid to 1 vol. of water).

C. S.

A Hydrocarbon of the *cyclo*Butane Series. Edgar Wedekind and M. Miller (*Ber.*, 1911, **44**, 3285—3287).—An account of the synthesis of 1 : 1 : 3 : 3-tetramethyl-2 : 4-diethyl*cyclo*butane.

1 : 1 : 3 : 3-*Tetramethyl*-2 : 4-*diethyl*cyclo*butane*-2 : 4-*diol*,

$$OH{\cdot}CEt{<}{}^{CMe_2}_{CMe_2}{>}CEt{\cdot}OH,$$

obtained by the interaction of magnesium ethyl bromide and tetramethyl*cyclo*butane-2 : 4-dione (Wedekind and Weisswange, Abstr., 1906, i, 437 ; Staudinger and Klever, *ibid.*, i, 234) is an oil, having an aromatic odour, b. p. 128—130°/30 mm., and reacts with hydriodic acid to form the corresponding *di-iodo*-compound, which on account of its instability could not be obtained in a pure condition. When reduced with zinc and glacial acetic acid, this yields 1 : 1 : 3 : 3-*tetramethyl*-2 : 4-*diethyl*cyclo*butane*, $CHEt{<}{}^{CMe_2}_{CMe_2}{>}CHEt$, which is a colourless, mobile liquid, b. p. 124—125°, and resembles in its chemical behaviour a saturated hydrocarbon of great stability.

1 : 1 : 3 : 3-*Tetramethyl*cyclo*butane*-2 : 4-*diol*, obtained in small yield by the reduction of tetramethyl*cyclo*butane-2 : 4-dione with sodium amalgam, and purified by means of its *diacetyl* derivative, is also mentioned.

F. B.

The *cyclo*Octane Series. V. *cyclo*Octatetraene. Richard Willstätter and Ernst Waser (*Ber.*, 1911, **44**, 3423—3445. Compare Abstr., 1905, i, 515 ; 1907, i, 303 ; 1908, i, 407 ; 1910, i, 366).—α-Dedimethylgranatenine, $C_8H_{11}NMe_2$, was prepared by distilling in a vacuum the quaternary base obtained from *n*-methylgranatenine. It unites with methyl iodide to form a quaternary ammonium iodide, the hydroxide of which, on distillation, yields *cyclo*octatriene. Two series of attempts were made to prepare *cyclo*octatetraene from this. In the first series bromine was added, and the dibromo*cyclo*octadiene so formed heated with quinoline. In this manner a hydrocarbon of the formula C_8H_8 was obtained, which, however, on reduction in the presence of platinum black yielded a mixture of di*cyclo*octane (C_8H_{14}) and tri*cyclo*octane (C_8H_{12}), thus showing that bridged rings had been formed during its preparation, probably owing to the rather high temperature employed. The second method was more successful. Dibromo*cyclo*octadiene was converted into tetramethyldiamino*cyclo*octadiene. When the quaternary base obtained from this was heated in the vacuum of a Geryk oil pump, it was split up into trimethyl-

amine and *cyclo*octatetraene. When the distillation was carried out in the vacuum of a water-pump, the hydrocarbon formed contained considerable quantities of a dicyclic impurity.

*cyclo*Octatetraene, in the presence of platinum black, readily unites with 4 molecules of hydrogen. It readily reduces permanganate and absorbs bromine. On treatment with nitrosulphuric acid it becomes resinified, but yields no nitro-derivative. It passes into more stable isomerides by the formation of bridged rings.

The contrast between the properties of *cyclo*octatetraene and benzene leads to a criticism of the formulæ proposed for the latter substance. The benzene formulæ of Kekulé and Thiele do not express these differences. The authors therefore prefer the centric benzene formula of Armstrong and von Baeyer, and consider that the centric equilibrium of the fourth carbon valencies does not occur in the case of an eight-carbon ring because the distance of the carbon atoms from the centre is greater than in the case of rings of six-carbon atoms. Having preferred the centric formula for benzene, the authors are led to propose the appended formula for naphthalene.

The authors have also prepared β-dedimethylgranatenine by complete methylation of methylgranatenine. When treated with hydrochloric acid, it yields granatal (Δ^2-*cyclo*octenone), together with a new base which has not been fully investigated.

N-Methylgranatenine was prepared by heating *N*-methylgranatoline with acetic acid and concentrated sulphuric acid at 180°. It crystallises readily, and has m. p. 17·2—17·4°, b. p. 62—62·2°/9 mm., and 186—186·5°/732 mm. Ciamician and Silber (Abstr., 1894, i, 154) give the b. p. 186°. It has D_4^{20} 0·961. Its *picrate*, which decomposes at 286°, *platinichloride*, m. p. 221° (decomp.), and *methiodide* were examined.

α-Dedimethylgranatenine, $C_8H_{11}NMe_2$, obtained by distilling the *quaternary ammonium base* from *N*-methylgranatenine under diminished pressure, is a colourless oil, which has b. p. 71—71·5°/8 mm., D_4^0 0·925, D_4^{20} 0·910. When heated at the ordinary pressure, it becomes transformed into the β-base. Its *platinichloride* has m. p. 168—169°, and decomposes at a higher temperature. The *methiodide* melts at 172—173° (decomp.).

β-Dedimethylgranatenine was prepared by the complete methylation of methylgranatenine. It is a colourless oil, b. p. 218—220°/721 mm. When exposed to air it become brown and gradually deposits a resin. On treatment with hydrochloric acid, it yields a base which has not been completely examined, together with granatal (Δ^2-*cyclo*octenone) (compare Ciamician and Silber, Abstr., 1894, i, 154). The constitution of the latter follows from its reduction to *cyclo*-octanone. The latter has b. p. 78·6—78·8°/13 mm. and 200—202° (corr.)/713 mm. It crystallises readily, and has m. p. 29·5°, which, by spreading on clay, is raised to 32·3—32·8°. Wallach (Abstr., 1907, i, 602) gives the m. p. 25—26°.

cyclo*Octatriene*, obtained by distillation of the quaternary base derived from α-dimethylgranatenine under diminished pressure, is a colourless, mobile oil, b. p. 147·2—148·2(corr.)/ordinary pressure,

31·2—31·8°/8 mm., and 33·5°/11 mm. Its density is much greater than that of *cyclo*octadiene, and somewhat higher than that of tropilidene. It has n_C^{20} 1·52281, n_D^{20} 1·52810, n_F^{20} 1·54131, and n_G^{20} 1·55322. On reduction with hydrogen in the presence of platinum black, it yielded *cyclo*octane, b. p. 149—150·3° (corr.), m. p. 11·6—11·8°. A former pure preparation had m. p. 14° (Abstr., 1910, i, 366). On oxidation with concentrated nitric acid, it yielded only pure hexane-$\alpha\zeta$-dicarboxylic acid.

*Dibromo*cyclo*octadiene* was prepared by mixing chloroform solutions of *cyclo*octatriene and bromine. On evaporation of the solvent in a vacuum, the dibromide remains as a faintly brown-coloured mass, which appears to undergo a certain amount of transformation when distilled under diminished pressure. It has b. p. 129·5—130°/9 mm., 136—137·5°/14 mm. It is very susceptible to the action of air. When heated with dimethylamine it yields *tetramethyldiamino*cyclo-*octadiene*, together with *dimethylamino*cyclo*octatriene*. The latter can be readily isolated by fractional distillation, and has b. p. 81—91°/10 mm., D_4^0 0·946, D_4^{20} 0·936. Its *platinichloride* has m. p. 200° (decomp.), and its *methiodide*, m. p. 224—225° (decomp.).

Tetramethyldiamino*cyclo*octadiene is best prepared by the action of dimethylamine on the undistilled *dibromo*cyclo*octadiene* dissolved in benzene. It is a pale yellow oil, which, on exposure to air, rapidly becomes dark brown. It has b. p. 126—127°/14 mm., D_4^0 0·944, D_4^{20} 0·935. The product was probably not quite pure. Its *platinichloride* darkens at 210° and decomposes at 220°. Its *methobromide* has m. p. 195—196° (decomp.), and its *methiodide*, m. p. 170—171° (decomp.).

The *platinichloride* of the *diammonium* base, $C_8H_{10}(NMe_3)_2Cl_6Pt$, has no definite melting point, but darkens at 225°.

On reduction, tetramethyldiamino*cyclo*octadiene passes into *tetramethyldiamino*cyclo*octane*, a pale yellow oil, b. p. 259—261°/718 mm., D_4^0 0·926, D_4^{20} 0·913.

By cautiously heating dibromo*cyclo*octadiene with quinoline, a *hydrocarbon* was obtained, which had the following constants: b. p. 31·6—32·8°/10 mm., 142·8—143·8°/737 mm., D_4^0 0·927, D_4^{20} 0·912, n_C^{20} 1·53460, n_D^{20} 1·54107, n_F^{20} 1·55764, n_G^{20} 1·57243. Analyses agreed with the formula C_8H_8, but the substance is probably not uniform, since, on reduction by hydrogen in the presence of platinum, it yields a mixture of approximately equal quantities of di*cyclo*octane (C_8H_{14}) and tri*cyclo*octane (C_8H_{12}). The reduced hydrocarbon has b. p. 136°/728 mm.

For the preparation of cyclo*octatetraene*, the quaternary ammonium base of tetramethyldiamino*cyclo*octadiene was distilled in the vacuum of a Geryk oil pump. In this case a temperature of 85—95° sufficed for decomposition of the base, whilst, when a water pump was used, heating had to be continued to 110°. The hydrocarbon was obtained as a yellow oil of sweet, powerful odour. When exposed to air it deposits amorphous, white particles. Two specimens boiled at 36·2—36·4°/14 mm. and 42·2—42·4°/17 mm. respectively. It has D_4^0 0·943, D_4^{20} 0·925, n_D^{20} 1·5389. On reduction with hydrogen in the presence of potassium black, it yields *cyclo*octane, b. p. 145—147°/720 mm., D_4^0 0·855, D_4^{20} 0·841. Pure *cyclo*octane has b. p. 147—148°/

720 mm. and D_4^{20} 0·839. Since the *cyclo*octane also could not be crystallised, it was not perfectly pure. On oxidation it yielded hexane-$\alpha\zeta$-dicarboxylic acid.

*cyclo*Octatetraene was kept for three days and then reduced as above. The *cyclo*octane formed was found to contain di*cyclo*octane. The reduction of *cyclo*octatetraene, obtained by heating the quaternary base in the vacuum of a water pump, yielded still more unsatisfactory results. The product was a mixture of much di*cyclo*octane with but little *cyclo*octane. H. W.

Two Methods of Treating the Problem of Substitution in the Benzene Nucleus. ARNOLD F. HOLLEMAN (*Ber.*, 1911, **44**, 3556—3562).—Mainly polemical. A reply to Obermiller (Abstr., 1911, i, 960). Holleman has based his laws of substitution on a study of the complete literature, showing that the position taken by a second substituting group in the benzene nucleus depends on the group already present, and, with but few exceptions, not on the nature of the entering group. This is also the case with a third substituting group.
E. F. A.

Propenylbenzene from Cinnamylammonium Salts. HERMANN EMDE (*Ber.*, 1911, **44**, 3224—3226).—Propenylbenzene, CHPh:CHMe, has been obtained by the reduction of quaternary cinnamylammonium salts with sodium amalgam (Emde, Abstr., 1909, i, 708) with a b. p. as high as 176—177°. The possibility of the material so prepared containing allylbenzene or propylbenzene is considered; it was divided into four fractions, and each of these decomposed by ozone. In no case was phenylacetaldehyde or phenylacetic acid obtained, all four fractions yielding benzaldehyde or benzoic acid. Allylbenzene was, therefore, not present. E. F. A.

Simultaneous Formation of Isomeric Substitution Products of Benzene. XVI. The Introduction of a Second Halogen Atom into Monohalogenated Benzenes. ARNOLD F. HOLLEMAN and T. VAN DER LINDEN (*Rec. trav. chim.*, 1911, **30**, 305—380).—The authors have studied the chlorination of monochloro- and monobromobenzene, and their bromination also, directing the reaction so that only one halogen atom enters the benzene nucleus. The amount of each isomeride formed has been estimated, and the effect of certain catalytic agents ($AlCl_3$, $FeCl_3$) on the proportions of the isomerides formed has also been studied.

The method employed for the quantitative estimation of the isomeric dihalogenated benzenes in their mixture from the halogenation consisted in (1) fractional distillation in a jacketed distilling flask, whereby almost all the unaltered monohalogenbenzene is removed. The residue is treated with 95·2% sulphuric acid, whereby the last trace of monohalogenbenzene is removed, whilst the dihalogenbenzene is unattacked by acid of this strength. It is essential that the acid be exactly this strength. This leaves behind a ternary mixture of the ortho-, meta-, and para-dihalogenbenzenes, the percentage of each isomeride being calculated after determining the initial point of solidification, when the para separates, and the second point of solidification, when the

whole mixture solidifies. Knowing these two values, the amounts of each isomeride in the mixture can be determined from tables and curves constructed previously from known mixtures of the pure substances.

Chlorobenzene was chlorinated at a temperature of 60—65°, slightly more than half the theoretical amount of chlorine being employed. In one set of experiments aluminium chloride was the catalyst, and in another ferric chloride. The amounts of the three isomerides present in the mixture differed considerably from the values given by Mouneyrat and Pouret (Abstr., 1899, i, 263). Only about 5·5% of the meta-compound was found, and its presence was confirmed by sulphonating the mixture, separating the barium salts of the sulphonic acids by fractional crystallisation, and from these preparing and identifying the corresponding sulphonamides. Two interesting microcrystalline reactions are quoted: one with rubidium chloride given by both the meta- and para-barium salts, and the other with sodium chloride given only by the para-salt.

Similar experiments were conducted with chlorine on bromobenzene and bromine on chloro- and bromo-benzene. For the removal of the last traces of bromobenzene a slightly different strength of sulphuric acid (95%) must be employed to that for chlorobenzene (95·2%).

It was found that the results obtained in different experiments, using aluminium chloride as catalyst, were not always in agreement. This is due to the fact that the aluminium chloride attacks the halogenated benzenes to a greater or less extent, and some benzene is produced. This is not the case with ferric chloride.

In chlorinating chloro- or bromo-benzene, aluminium favours the formation of the para-isomeride, iron, on the other hand, favouring the formation of the ortho. In bromination the reverse is the case. Without a catalyst the amounts of products obtained are situated between those with aluminium and those with iron. The substituent present in the compound has very little influence on the reaction, but the substituent entering seems to exert a great influence on the amounts of the three isomerides obtained. The amounts of ortho- and meta-isomerides seem to increase or diminish together, as opposed to the para-isomeride. W. G.

6-Iodo-1-methyl-3-ethylbenzene and its Derivatives containing Multivalent Iodine. CONRAD WILLGERODT and MAX JAHN (*Annalen*, 1911, **385**, 328—340).—By the usual method, 5-ethyl-*o*-toluidine is converted into 6-*iodo*-1-*methyl*-3-*ethylbenzene*, C_6H_3MeEtI, b. p. 242°, which reacts with chlorine in cold acetic acid to form 2-*methyl*-4-*ethylphenyl iododichloride*, $C_6H_3MeEt\cdot ICl_2$, yellow needles. 6-*Iodoso*-1-*methyl*-3-*ethylbenzene*, $C_6H_3MeEt\cdot IO$, decomp. 162°, obtained from the iododichloride and 10% sodium carbonate, forms a *diacetate*, $C_6H_3MeEt\cdot I(OAc)_2$, m. p. 104°, and is converted by distillation with steam into 6-*iodoxy*-1-*methyl*-3-*ethylbenzene*, $C_6H_3MeEt\cdot IO_2$, which explodes at 161°. Equal molecular quantities of the iodoso- and the iodoxy-compounds react with silver oxide and water at 40—50° to form ultimately a solution of *di*-2-*methyl*-4-*ethylphenyliodonium hydroxide*, $OH\cdot I(C_6H_3MeEt)_2$, from which the *chloride*, m. p. 148°, *platinichloride*, m. p. 163°, *mercurichloride*, m. p. 109—110°, *bromide*,

m. p. 162°, *iodide*, m. p. 134°, *nitrate*, m. p. 150° (decomp.), and *dichromate*, decomp. 132°, have been prepared. *Iododi-2-methyl-4-ethylphenyliodonium hydroxide*, $C_6H_3MeEt\cdot I(OH)\cdot C_6H_2MeEtI$, the *sulphate* of which is obtained by the careful addition of the preceding iodoso-compound to concentrated sulphuric acid cooled by a freezing mixture, forms a *chloride*, m. p. 88°, *platinichloride*, m. p. 110—111° (decomp.), *mercurichloride*, m. p. 87°, *bromide*, m. p. 101°, *iodide*, m. p. 82°, and *dichromate*, m. p. 52°, resolidifying at 87°. o-*Tolyl-2-methyl-4-ethylphenyliodonium hydroxide*, $C_6H_4Me\cdot I(OH)\cdot C_6H_3MeEt$, obtained in solution from *o*-iodoxytoluene and 6-iodoso-1-methyl-3-ethylbenzene and moist silver oxide, forms a *chloride*, m. p. 174°, *platinichloride*, m. p. 174° (decomp.), *mercurichloride*, m. p. 133°, *bromide*, m. p. 167°, *iodide*, decomp. 135°, and *dichromate*, decomp. about 138°.

2-*Methyl-4-ethylphenyldichlorovinyliodonium chloride*,

$$C_6H_3MeEt\cdot ICl\cdot C_2HCl_2,$$

m. p. 144°, obtained by triturating 5-ethyl-*o*-tolyl iododichloride and acetylene silver chloride with water (compare Thiele and Haakh, Abstr., 1909, i, 865), has been converted into the *platinichloride*, *mercurichloride*, m. p. 67°, *bromide*, m. p. 126°, *iodide*, decomp. 71°, *nitrate*, m. p. 93—94°, *hydrogen sulphate*, m. p. 56°, and unstable *dichromate*. C. S.

5-Iodo-ψ-cumene and its Derivatives. CONRAD WILLGERODT and ROBERT MEYER (*Annalen*, 1911, **385**, 341—351).—5-*Iodo-ψ-cumene*, $C_6H_2Me_3I$, m. p. 37°, is most conveniently prepared by heating on the water-bath a mixture of ψ-cumene in petroleum, sulphur iodide, and nitric acid, D 1·34. It yields the following derivatives containing multivalent iodine. ψ-*Cumyl iododichloride*, $C_6H_2Me_3\cdot ICl_2$, decomp. 66°; 5-*iodoso-ψ-cumene*, $C_6H_2Me_3\cdot IO$, decomp. 171° (*acetate*, m. p. 123°); 5-*iodoxy-ψ-cumene*, $C_6H_2Me_3\cdot IO_2$, explodes at 210°; *di-ψ-cumyliodonium chloride*, $(C_6H_2Me_3)_2ICl$, m. p. 107°, and the corresponding *platinichloride*, m. p. 159°, *aurichloride*, m. p. 90°, *bromide*, m. p. 118°, *iodide*, m. p. 120°, and *dichromate*, exploding at 120°; 5-*iodo-di-ψ-cumyliodonium chloride*, $C_6H_2Me_3\cdot ICl\cdot C_6HMe_3I$, m. p. 106°, and the corresponding *platinichloride*, m. p. 150°, *mercurichloride*, m. p. 108°, *aurichloride*, *bromide*, m. p. 105°, *iodide*, m. p. 112°, and *dichromate*, decomp. 113°; *phenyl-ψ-cumyliodonium chloride*, m. p. 186°, and the corresponding *platinichloride*, *aurichloride*, m. p. 117°, *mercurichloride*, m. p. 161°, *bromide*, m. p. 173°, *iodide*, decomp. 147°, and *dichromate*, exploding at 184°; p-*tolyl-ψ-cumyliodonium chloride*, m. p. 171°, and the corresponding *platinichloride*, *aurichloride*, m. p. 71°, *mercurichloride*, m. p. 81°, *bromide*, m. p. 148°, *iodide*, decomp. 108°, and *dichromate*, decomp. 149°; ψ-*cumyldichlorovinyliodonium chloride*,

$$C_6H_2Me_3\cdot ICl\cdot C_2HCl_2,$$

m. p. 169°, and the corresponding *platinichloride*, *aurichloride*, m. p. 134° approx., *bromide*, m. p. 131°, and *iodide*, m. p. 96°.

When chlorine is passed into an uncooled solution of 5-iodo-ψ-cumene in chloroform, the product is 4 : 6-*dichloro-5-iodo-ψ-cumene*, $C_6Me_3Cl_2I$, m. p. 188—189°; derivatives of this, containing multivalent iodine, cannot be prepared. C. S.

Nitroalkylates. IWAN OSTROMISSLENSKY (*J. pr. Chem.*, 1911, [ii], **84**, 495—506. Compare this vol., i, 1).—The colorations produced by

the addition of aliphatic nitro-compounds to organic substances containing ethylenic linkings are due probably to members of a new class of additive compounds, which are analogous to the picrates and which the author proposes to call nitroalkylates.

The tetranitromethanates of pyrene, acenaphthene, anthracene, and naphthalene are relatively the most stable, and are precipitated together with their components by the addition of water to their dilute alcoholic solutions. The cryoscopic behaviour of their dilute solutions in nitrobenzene indicates that the tetranitromethanates are almost completely dissociated into their components.

Reasons are advanced for ascribing the constitution :

$$R{<}\begin{matrix} NO_2 \cdots -CR' \\ \qquad\qquad | \\ NO_2 \cdots -CR'' \end{matrix}$$

to the nitroalkylates. The following are described: *anthranilic acid* 1 : 3 : 5 - *trinitrobenzenate*, $NH_2{\cdot}C_6H_4{\cdot}CO_2H,C_6H_3(NO_2)_3$, m. p. 186—187°, orange needles ; *aminoazobenzene* 1 : 3 : 5-*trinitrobenzenate*, $NH_2{\cdot}C_6H_4{\cdot}N{:}NPh,C_6H_3(NO_2)_3$, m. p. 156—157°, orange leaflets ; *phenylhydrazine* 1 : 3 : 5 - *trinitrobenzenate*, $NHPh{\cdot}NH_2,C_6H_3(NO_2)_3$, orange needles ; *fluorene* β-1 : 3 : 6 : 8-*tetranitronaphthalenate*,

$$C_{13}H_{10},2C_{10}H_4(NO_2)_3,$$

m. p. 154—155°, brownish-yellow needles ; *aniline* p-*hydroxynitrobenzenate*, $PhNH_2,NO_2{\cdot}C_6H_4{\cdot}OH$, m. p. 41—42°, pale yellow prisms.

A list is given of nineteen substances which unite with 2 molecules of picric acid or other nitro-compound. It is claimed that the molecules of the picric acid, picryl chloride, trinitrobenzene, tetranitronaphthalene, or other nitro-compound are combined, not with the whole complex of the ethylenic molecule, but at a definite portion thereof, namely, at the ethylenic linking. It is shown, by Zerewitinoff's method with magnesium methyl iodide, that the NH_2 or NH groups in nitroalkylates containing such groups do not experience any change, and still retain two and one active hydrogen atoms respectively.

C. S.

ακ-Diphenyldecane and the Preparation of ωω′-Diarylated Fatty Hydrocarbons. WALTHER BORSCHE and J. WOLLEMANN (*Ber.*, 1911, **44**, 3185—3188).—Sebacyl chloride combines with benzene to form diphenyldecanedione, $COPh{\cdot}[CH_2]_8{\cdot}COPh$ (Auger, *Ann. Chim. Phys.*, 1891, [vi], **22**, 361), in presence of aluminium chloride, ω-benzoylnonoic acid, m. p. 85—86° (Auger, *loc. cit.*), being also formed. The dioxime of the ketone is readily reduced by sodium to the diamine, which on distillation of its phosphate forms ακ-diphenyl-$\Delta^{\alpha\iota}$-decadiene ; this, when shaken in methyl-alcoholic solution with colloidal palladium and hydrogen, is reduced to ακ-diphenyl-*n*-decane.

ακ - Dioximino - ακ - diphenyldecane, $OH{\cdot}N{:}CPh{\cdot}[CH_2]_8{\cdot}CPh{:}N{\cdot}OH$, forms yellowish-white crystals, m. p. 120—121° ; it slowly decomposes when kept.

ακ-Diamino-ακ-diphenyldecane is a colourless oil, b. p. 260°/18 mm., with a characteristic basic odour ; the *dibenzoate* forms a colourless powder, m. p. 198—199°. *Dicarbamidodiphenyl decane* separates in microscopic needles, m. p. 183—184°. *ακ - Diphenyl-$\Delta^{\alpha\iota}$-decadiene*, $CHPh{:}CH{\cdot}[CH_2]_6{\cdot}CH{:}CHPh$, forms large needles, m. p. 53°. With

two molecules of bromine, *αβικ-tetrabromo-ακ-diphenyldecane* is obtained as a colourless, crystalline mass, m. p. 164—165°.

ακ-Dihydroxy-ακ-diphenyldecane, $OH\cdot CHPh\cdot[CH_2]_8\cdot CHPh\cdot OH$, obtained by reduction of diphenyldecanedione with sodium and ethyl alcohol, forms colourless, matted needles, m. p. 70—72°.

*ακ-Diphenyl-*n*-decane* is a transparent, strongly refractive oil, b. p. 234°/12 mm., solidifying to colourless crystals, m. p. 16—17°.

E. F. A.

Some Secondary Aromatic Amines Related to Di*iso*propylamine. M. C. de Leeuw (*Rec. trav. chim.*, 1911, **30**, 239—269).—The behaviour of some secondary amines, in which one or more of the methyl groups of di*iso*propylamine are replaced by phenyl, as compared with that of di*iso*propylamine itself, has been studied. The amines experimented with were α-phenylethyl*iso*propylamine, di-α-phenylethylamine, diphenylmethyl*iso*propylamine, diphenylmethyl-α-phenylethylamine, and di-diphenylmethylamine. These were all prepared by Hofmann's method, namely, the condensation of an alkyl halide (1 mol.) with an amine (2 mols.).

*α-Phenylethyl*iso*propylamine*, $CHMePh\cdot NH\cdot CHMe_2$, is obtained by heating together α-phenylethylamine (2 mols.) and *iso*propyl iodide (1 mol.) in sealed tubes at 100°. The *hydrochloride* forms colourless crystals, m. p. 235·5°. By treatment with potassium hydroxide, it yields the *base*, a colourless, mobile liquid, b. p. 90·5—92°/20 mm., D_4^{14} 0·905, n_D^{14} 1·4996. The *picrate* has m. p. 157·5°. The *nitrite*, m. p. 122°, when warmed with water, yields the corresponding *nitrosoamine*, a pale yellow liquid, b. p. 162°/19 mm., $D_4^{15\cdot7}$ 1·034, $n_D^{15\cdot7}$ 1·52657.

Di-α-phenylethyl-amine, $NH(CHMePh)_2$ (compare Busch and Leefhelm, Abstr., 1908, i, 151), was obtained from α-phenylethylamine and α-phenylethyl bromide. With sodium nitrite, it yields a nitrosoamine, which was not, however, isolated.

*Diphenylmethyl*iso*propylamine*, $CHPh_2\cdot NH\cdot CHMe_2$, is prepared by the condensation of diphenylmethylamine and *iso*propyl iodide as a highly refractive, colourless liquid, which crystallises on cooling, m. p. 11·5°, b. p. 181·5—182°/25 mm., D_4^{13} 1·001, n_D^{13} 1·56015. It yields a *hydrochloride*, m. p. 213—214°, which crystallises from water with $1H_2O$. The *nitrite*, m. p. 107°, is very unstable, decomposing if heated in benzene solution above 55°, and yielding if heated to fusion the corresponding *nitrosoamine*, m. p. 75°. The *picrate* has m. p. 189—190°, and *acetyl* derivative, m. p. 89·5°.

Diphenylmethyl-α-phenylethylamine, $CHPh_2\cdot NH\cdot CHMePh$, results from the condensation of α-phenylethylamine and diphenylmethyl bromide. It is a colourless liquid, b. p. 234·5—235°/19 mm., $D_4^{13\cdot6}$ 1·060, $n_D^{13\cdot6}$ 1·59824, and yields a *hydrochloride*, m. p. 232·5—234°. No nitrite could be isolated, but from a solution of the hydrochloride in absolute alcohol by treatment with sodium nitrite, the *nitrosoamine*, m. p. 80·5°, was obtained. The *picrate*, m. p. 184·5°, crystallises with 1 mol. of benzene.

Di-diphenylmethyl-amine, $NH:(CHPh_2)_2$ (compare Friedel and Balsohn, Abstr., 1881, 279), was obtained by the action of diphenylmethylamine on diphenylmethyl bromide. The *hydrochloride* has m. p. 200—202°.

It is noticeable that the melting points, boiling points, specific gravities, and refractive indices of the bases rise as the base contains more phenyl and fewer methyl groups. The basic character diminishes with increase in the number of phenyl groups in the substance, as is shown by the stability of the hydrochlorides and nitrites towards water. None of the bases yielded a picryl derivative with picryl chloride, thus resembling di*iso*propylamine itself. W. G.

Optically Active Amino-oxides. JAKOB MEISENHEIMER (*Annalen*, 1911, **385**, 117—155).—The existence of substances of the type ***a***: N *bcd* in enantiomorphous configurations, previously exemplified by the methylethylaniline oxides (Abstr., 1909, i, 20), has been substantiated by the isolation of the active forms of β-naphthylmethylethylamine oxide and of kairoline oxide. According to Jones (Trans., 1903, **83**, 1400; 1907, **91**, 1821), substances of the type >C : N *bcd* exist in only one form. The author suggests that in these cases the double linking stands in the place of two of the non-ionisable groups, whilst in the amino-oxides it is in the place of the linking binding the acid group and one of the other four linkings (*loc. cit.*).

Further information is given regarding the methylethylaniline oxides. The *d*-base is obtained most conveniently by resolving the racemic base by means of *d*-tartaric acid. The active and the racemic modifications of the base have been obtained anhydrous and crystalline; their composition corresponds with the formula: O⁚NMeEtPh. The active forms have $[M]_D \pm 24°$ in 1—2% aqueous solution, and $\pm 8°$ in 1—2% benzene solution. d-*Hydroxyphenylmethylethylammonium* d-*tartrate*, $C_9H_{13}ON,C_4H_6O_6$, has m. p. 134—135° and $[M]_D$ 81·9° in alcohol.

[With MARTHA HOFFHEINZ.]—r-β-*Naphthylmethylethylamine oxide*, $O⁚NMeEt\cdot C_{10}H_7,3H_2O$, m. p. 70°, colourless leaflets, is obtained by oxidising methylethyl-β-naphthylamine by Caro's acid at the ordinary temperature. It is not resolved by *d*-bromocamphorsulphonic acid; the *bromocamphorsulphonate* obtained has decomp. 135°, after repeated crystallisation, and $[M]_D + 282°$, as against the initial value $+273°$. The resolution is accomplished by means of the tartaric acids. The racemic base and *d*-tartaric acid in alcoholic solution yield d-*hydroxy*-β-*naphthylmethylethylammonium* d-*tartrate*, $C_{13}H_{15}ON,C_4H_6O_6$, m. p. 132—135°, decomp. 135°, $[M]_D + 107·8°$, whilst l-*hydroxy*-β-*naphthylmethylethylammonium* l-*tartrate*, obtained in a similar manner by means of *l*-tartaric acid, has m. p. 132—135°, decomp. 135°, and $[M]_D - 107·8°$ in aqueous solution. Each of these tartrates is converted through the *picrate*, decomp. 118—119°, and the *chloride* into the free *base*,

$$C_{13}H_{15}ON,3H_2O,$$

m. p. 67—70°, needles; the *d*-base and the *l*-base have $[M]_D + 38°$ and $-39°$ respectively in aqueous solution.

[With JACOB DODONOW.]—Kairoline is oxidised by 3% hydrogen peroxide at 60—65° to r-*kairoline oxide*, $C_{10}H_{13}ON$, m. p. 124° (decomp.), which is isolated in the form of the *hydrochloride*, $C_{10}H_{13}ON,HCl$, m. p. 144° (decomp.) (*platinichloride*, m. p. 153° decomp.), or better as the *picrate*, m. p. 122° (decomp.). The resolution of the *r*-base is effected with extraordinary ease. An alcoholic solution is treated

with alcoholic *d*-tartaric acid, the crystals of l-*hydroxykairolinium* d-*tartrate* which are deposited in 90% yield, are removed, the filtrate is freed from the excess of *d*-tartaric acid by the addition of ammonium chloride, and is then concentrated and treated with aqueous ammonium *d*-bromocamphorsulphonate, whereby d-*hydroxykairolinium* d-*bromocamphorsulphonate* is obtained in 80% yield. This salt has decomp. 165° and $[M]_D$ +362°, and is converted as usual through the d-*picrate*, m. p. 126° (decomp.), and d-*chloride*, decomp. 138°, $[M]_D$ +88°, into d-*kairoline oxide*, $C_{10}H_{13}ON,H_2O$, hygroscopic plates, which has $[M]_D$ +45° in water and (anhydrous) +134° in benzene. l-*Hydroxykairolinium* d-*tartrate*, m. p. 145° (decomp), $[M]_D$ −48°, is converted through the l-*picrate*, m. p. 126° (decomp.), and l-*chloride*, decomp. 138°, $[M]_D$ −88°, into l-*kairoline oxide*, $C_{10}H_{13}ON,H_2O$, $[M]_D$ −45° in water and (anhydrous) −137° in benzene.

r-Kairoline oxide reacts with methyl iodide in the presence of methyl alcohol to form a *periodide*, $C_{10}H_{13}ONI_2$, decomp. 145°, dimethyltetrahydroquinolinium iodide, and kairoline; the last substance is optically inactive even when the experiment is performed with *l*-kairoline oxide. Similar products are obtained when methyl sulphate is used. C. S.

Salts and Esters of Alkylaminodithiocarbamic Acids. ERNEST FOURNEAU and VILA (*Bull. Soc. chim.*, 1911, [iv], 9, 985—989. Compare Abstr., 1911, i, 528).—It has been shown (Abstr., 1911, i, 528) that alkylaminoacetic acids react with carbon disulphide to give the corresponding dithiocarbamates. It is now shown that, if an arylaminoacetic acid is employed, the product is a thiothiazolone.

When ethyl or bromophenylacetate reacts with methylamine in benzene solution it yields *ethyl methylaminophenylacetate*, an oil readily saponified by boiling water, b. p. 136°/10 mm. This ester reacts in ether with carbon disulphide to form 2-thio-4-phenyl-3-methylthiazolone, $CHPh<\begin{matrix}NMe\cdot CS\\ CO—S\end{matrix}$, voluminous prisms, m. p. 137°. This, when treated with ammonia, does not yield the amide of the corresponding dithiocarbamic acid, but methylaminophenylacetamide. When warmed with sodium hydroxide in alcoholic solution, it yields the *sodium* derivative, $CO_2Na\cdot CHPh\cdot NMe\cdot CS_2Na$. The *potassium* derivative is prepared in a similar manner. If to a solution of the sodium salt in water freshly precipitated mercuric oxide is added, the unstable *compound*, $(CO_2Na\cdot CHPh\cdot NMe\cdot CS_2)_2Hg$, is precipitated in the form of pale yellow crystals. Organo-mercury compounds, such as mercuryaniline, behave in the same way as the mercuric oxide.

If a solution of antimony trichloride is added to a solution of the potassium salt in water, there results an ill-defined *compound*, which should theoretically be $(CO_2K\cdot CHPh\cdot NMe\cdot CS_2)_3Sb$, but, judged by the estimation of the antimony, seems to correspond more nearly with the formula $(CO_2K\cdot CHPh\cdot NMe\cdot CS_2)_2Sb\cdot OH$. This substance is of therapeutic interest. W. G.

Diamidothiophosphoric Acid. FRITZ EPHRAIM (*Ber.*, 1911, 44, 3414—3416. Compare Abstr., 1911, i, 284).—Diamidothiophosphoric

acid is obtained from the compound $PCl_2 \cdot OPh$ by the addition of sulphur, replacement of the chlorine atoms by the amino-group, and saponification of the resulting ester.

Phenyl dichlorothiophosphate, $PSCl_2 \cdot OPh$, is formed when the compound $PCl_2 \cdot OPh$ (1 mol.) is heated with sulphur (1 atom) for half an hour in a sealed tube at 220—230°. Fractional distillation of the product gives a colourless, highly refractive liquid, possessing a slight but unpleasant odour, b. p. 260° (decomp.) or 133°/22 mm. Owing to its insolubility in aqueous solutions, it is practically unacted on by dilute acids or concentrated sodium hydroxide. Nitric acid (D 1·4) gives rise to phenyl or else nitrophenyl phosphate. When dissolved in alcohol and treated with aqueous ammonia (D 0·82), crystals of *phenyl diamidothiophosphate*, $PS(NH_2)_2 \cdot OPh$, are readily obtained, m. p. 118°. This compound cannot be hydrolysed by boiling with aqueous sodium hydroxide. To bring about hydrolysis, it is necessary to mix it with 2·3 mols. of solid sodium hydroxide and add a few drops of water; the heat of solution of the sodium hydroxide starts the hydrolysis. Addition of acetic acid and alcohol then precipitates an oil, which is doubtless *diamidothiophosphoric acid*, $PS(NH_2)_2 \cdot OH$. It is very unstable, gradually decomposing with evolution of hydrogen sulphide, so that it could not be obtained pure. The *silver* salt is characteristic. T. S. P.

Hydrazidophosphoric Acid. FRITZ EPHRAIM and M. SACKHEIM (*Ber.*, 1911, **44**, 3416—3423).—In order to prepare monohydrazidophosphoric acid, $PO(OH)_2 \cdot N_2H_3$, the authors wished to nitrate amidophosphoric acid, $PO(OH)_2 \cdot NH_2$, and from the nitroamide so produced, obtain the hydrazide by reduction (compare the analogous process for the derivatives of sulphuric acid, Abstr., 1911, ii, 286). Since free amidophosphoric acid is very unstable, the nitration experiments were carried out with the phenyl ester, but it was found that nitration always took place in the phenyl group, the amido-group being split off at the same time. The following method was therefore used: Diphenyl chlorophosphate was transformed into the hydrazide, from which salts of hydrazidophosphoric acid could be obtained by saponification, in accordance with the scheme:

$$OP{<}^{(OPh)_2}_{Cl} \xrightarrow{N_2H_4} OP{<}^{(OPh)_2}_{NH \cdot NH_2} \xrightarrow{NaOH} OP{<}^{(ONa)_2}_{NH \cdot NH_2}.$$

Diphenyl hydrazidophosphate, $PO(OPh)_2 \cdot N_2H_3$, is obtained by the interaction of diphenyl chlorophosphate (1 mol.) and hydrazine hydrate (1 mol.) in alcoholic solution. A precipitate of the hydrochloride is first formed, and water is then added until the precipitate dissolves and the liquid becomes milky. On cooling, crystals of the desired compound are obtained, m. p. 112°. On hydrolysis with solid sodium hydroxide and a few drops of water (compare the previous abstract), *sodium phenyl hydrazidophosphate*,

$$OPh \cdot PO(ONa) \cdot N_2H_3,$$

is produced; it crystallises in needles from alcohol. The *disodium hydrazidophosphate*, $PO(ONa)_2 \cdot N_2H_3$, results when the reaction mixture is heated for ten minutes, after hydrolysis with the formation of the monosodium salt is complete. It is best prepared by hydrolysis

of the diphenyl ester with 25% sodium hydroxide under reflux. *Sodium hydrogen hydrazidophosphate*, $ONa\cdot PO(OH)\cdot N_2H_3$, on account of its sparing solubility, is precipitated from a solution of the normal salt by the careful addition of acetic acid. The *normal potassium* salt and the *potassium hydrogen* salt are prepared similarly to the sodium salts. *Ammonium* and *barium phenyl hydrazidophosphates*, $OPh\cdot PO(O\cdot NH_4)\cdot N_2H_3$ and $[PO(OPh)(N_2H_3)\cdot O]_2Ba$, are obtained from the diphenyl ester by hydrolysis with concentrated ammonium hydroxide and barium hydroxide respectively. Barium hydrazidophosphate could not be obtained pure. The *lead* salts of hydrazidophosphoric acid and of phenylhydrazidophosphoric acid are obtained by double decomposition of the corresponding sodium salts with lead acetate.

Free hydrazidophosphoric acid, as also its phenyl ester, were obtained in solution by interaction of the lead or barium salts with hydrogen sulphide or sulphuric acid. The solutions reduce silver nitrate and Fehling's solution with difficulty at the ordinary temperature, somewhat more quickly on boiling. The solid acids could not be isolated.

When diphenyl hydrazidophosphate is heated gradually to 150°, 1 mol. of hydrazine is lost from 2 mols. of ester, with the formation of *diphenyl hydrazidodiphosphate*,

$$OPh\cdot PO\cdot NH\cdot NH\cdot PO\cdot OPh.$$

This compound forms microscopic needles; it does not react with aldehyde, nor does it reduce alcoholic ammoniacal silver nitrate, so that it probably does not possess the formula $NH_2\cdot N[PO(OPh)_2]_2$. It is changed by boiling water in some way, the solution then readily reducing silver nitrate. When the hot alcoholic solution is precipitated with water, hydrazine is split off, the precipitate consisting of monophenyl phosphate, $PO(OH)_2\cdot OPh$ (compare Rapp, Abstr., 1884, 1337).

Nitration of diphenyl amidophosphate gives rise to a mixture of *o*- and *p*-dinitrophenyl phosphates, $OH\cdot PO(O\cdot C_6H_4\cdot NO_2)_2$, which melts to a turbid liquid at 95—97°, the fusion clearing suddenly at 165—167° (compare Rapp, *loc. cit.*). The mixture contains only a very small proportion of the ortho-compound (about 0·2%). *Sodium* p-*dinitrophenyl phosphate* forms light yellow, slender needles; the *silver* salt forms slender, white needles. T. S. P.

The Reactions of 4-Nitrosophenol, 2:6-Dibromo-4-nitrosophenol, and 6-Nitroso-*m*-cresol with Bromine. HENRI VAN ERP (*Rec. trav. chim.*, 1911, 30, 270—304. Compare Bridge, Abstr., 1894, i, 25; Raiford and Heyl, Abstr., 1910, i, 273, 730).—A determination of the products obtained by the action of bromine on solutions of phenol containing nitrosophenol. From his experiments the author draws the conclusion that, when nitrosophenol is treated with excess of bromine, the principal product is 2:4:6-tribromophenol, probably formed according to the equation: $NO\cdot C_6H_4\cdot OH + 8Br + 2H_2O = C_6H_2Br_3\cdot OH + HNO_3 + 5HBr$. Other products are 4:6-dibromo-2-nitrophenol, 2:6-dibromo-4-nitrophenol, and 2:6-dibromo-*p*-benzoquinone in small quantity.

2:6-Dibromo-4-nitrosophenol was prepared both from the nitroso-

phenol and bromine (Fischer and Hepp, Abstr., 1888, 456), and by the action of hydroxylamine on 2 : 6-dibromo-*p*-benzoquinone, and, contrary to Kehrmann's results (compare Abstr., 1889, 243), the products in the two cases were identical.

2 : 4 : 6-Tribromo-*m*-cresol yields an *acetate* and a *benzoate*, m. p. 87°.

The *diacetate* of 2 : 6-dibromoquinol is obtained in colourless prisms, m. p. 116·5° ; the *dibenzoate* has m. p. 136°.

Dibromodianilino-p-*benzoquinone* is obtained by the addition of aniline, dissolved in alcohol, to a warm solution of 2 : 6-dibromo-*p*-benzoquinone in alcohol. It forms an olive-coloured, microcrystalline powder, which does not melt at 300° (compare Niemeyer, Abstr., 1885, 1065).

By the action of bromine in excess on 4-nitrosophenol in alcoholic solution and subsequent distillation in steam, there resulted (1) a non-volatile product, which was shown to be 2 : 6-dibromo-4-nitrophenol ; (2) a volatile portion, which formed the major part of the products, and consisted chiefly of 2 : 4 : 6-tribromophenol with a little 4 : 6-dibromo-2-nitrophenol.

Working with water as a solvent instead of alcohol, the products were the same, but in this case some 2 : 6-dibromo-*p*-benzoquinone was also isolated. In each case the hydrogen bromide obtained from the reaction was in excess of the amount demanded by the equation. This the author considers was due to the formation of brominated resinous by-products and consequent generation of hydrogen bromide.

That the 2 : 6-dibromo-4-nitrophenol does not result by isomeric change from 4 : 6-dibromo-2-nitrophenol, or vice versa, in this reaction is shown by taking solutions of each of these separately in acetic acid, gradually adding sodium nitrite, and allowing the solutions to remain. After three days the starting materials can be recovered unchanged without any trace of the isomeride being present.

2 : 4 : 6-Tribromophenol is the product of the action of bromine in excess on an alcoholic solution of 2 : 6-dibromo-4-nitrosophenol. With 6-nitroso-*m*-cresol, bromine yields 2 : 4 : 6-tribromo-*m*-cresol.

W. G.

Action of Magnesium Ethyl Bromide on Anthraquinone. LATHAM CLARKE and PAUL WHITTIER CARLETON (*J. Amer. Chem. Soc.*, 1911, **33**, 1966—1973).—It has been shown by Clarke (Abstr., 1908, i, 330) that magnesium ethyl bromide reacts with anthraquinone with formation of 9 : 10-dihydroxy-9 : 10-diethyldihydroanthracene. A further study of this reaction has shown that when the magnesium ethyl bromide is in excess, dihydroxydiethyldihydroanthracene is formed, but that when the anthraquinone is in excess, ethyloxanthranol is produced.

9 : 10-Dihydroxy-9 : 10-diethyldihydroanthracene has m. p. 172°, and its *dimethyl ether*, m. p. 178° ; the *diethyl ether* has also been prepared. When the compound is treated with acetyl chloride, a cream-coloured *substance*, $C_{16}H_{17}O$, m. p. 135·5—136°, is produced which crystallises in needles and dissolves in methyl alcohol to form a solution with a blue fluorescence. By the action of zinc dust and glacial acetic acid, the dihydroxy-compound is converted into diethyl-

anthracene. When the compound is heated with dilute hydrochloric acid, a mixture of two isomeric *substances*, $C_{36}H_{34}O$, is obtained. One of these compounds, probably $\left(CHMe{:}C{<}{}^{C_6H_4}_{C_6H_4}{>}CEt\right)_2O$, m. p. 161°, forms yellow, rhombic plates, and the other, possibly

$$\left(CHMeEt{\cdot}C{<}{}^{C_6H_4}_{C_6H_4}{>}C\right)_2O,$$

m. p. 226°, crystallises in yellow prisms, and gives fluorescent solutions. These substances are also formed as by-products in the preparation of 9 : 10-dihydroxy-9 : 10-diethyldihydroanthracene. E. G.

Synthesis of Butein. A. Göschke and J. Tambor (*Ber.*, 1911, **44**, 3502—3505).—The authors will describe shortly a method of synthesising polyhydroxychalkones. Amongst others, butein (Perkin and Hummel, Trans., 1904, **85**, 1459) has been obtained by treating a boiling alcoholic solution of equal molecular quantities of protocatechualdehyde and resacetophenone with 50% potassium hydroxide. The product, which is obtained by acidification and purified through the tetra-acetyl derivative, is shown to be identical with natural butein by direct comparison. The 4′ : 5′-*methylene ether*,

$$C_6H_3(OH)_2{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_3{<}{}^{O}_{O}{>}CH_2,$$

m. p. 185°, yellow needles, prepared in a similar manner from piperonal and resacetophenone, yields 2 : 4-*dimethoxy*-4′ : 5′-*dioxymethylenechalkone*, m. p. 168°, by treatment with warm methyl sulphate and 50% potassium hydroxide. C. S.

***a-iso*Dypnopinacolin.** Maurice Delacre (*Bull. Soc. chim.*, 1911, [iv], **9**, 1024—1025).—In this preliminary communication it is shown that dehydrodypnopinacolin, $C_{32}H_{24}O$, can be obtained by the oxidation of *a-iso*dypnopinacolin, $C_{32}H_{26}O$, with bromine (compare Abstr., 1896, i, 662). Oxidation with chromic acid in acetic acid gives rise to dehydrodypnopinacone, $C_{32}H_{26}O_2$. The latter by dehydration furnishes dehydrodypnopinacolin, and this on treatment with sodium amalgam gives a *substance*, $C_{32}H_{26}O$, isomeric with dypnopinacolin, but which behaves as an alcohol, and with acetyl chloride gives a hydrocarbon, which may be *iso*dypnopinacolene (da Costa, Thèse, 1911). T. A. H.

Cholesterol. III. Leo Tschugaeff and P. Koch (*Annalen*, 1911, **385**, 352—358. Compare Abstr., 1910, i, 734).—Recently several investigations of the behaviour of cholesterol and its immediate derivatives towards ozone (Molinari and Fenaroli, Abstr., 1908, i, 882; Dorée, Trans., 1909, **95**, 638; Diels and Abderhalden, Abstr., 1904, i, 880; Diels, *ibid.*, i, 728) have thrown doubt on the usually accepted view that the molecule of cholesterol contains only one ethylenic linking. The authors, therefore, have determined the molecular refractions of cholesterol, cholestane, cholestene, α-cholesterylene, methyl cholesterylxanthate, and methyl dihydrochol-

esterylxanthate in benzene, and have obtained values which agree closely with those calculated on the assumption that only one ordinary ethylenic linking is present in the molecule of cholesterol.

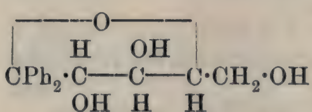
C. S.

Synthesis of $\alpha\alpha$-Diaryl Substituted Arabitol. CARL PAAL and MAX KINSCHER (*Ber.*, 1911, **43**, 3543—3555. Compare Abstr., 1906, i, 802).—On treatment of triacetyl-*l*-arabonolactone with magnesium phenyl bromide and decomposition of the product with dilute acids, $\alpha\alpha$-diphenyl-*l*-arabitol is obtained. In a similar manner, $\alpha\alpha$-di-*p*-tolyl- and $\alpha\alpha$-dibenzyl-arabitols have been prepared.

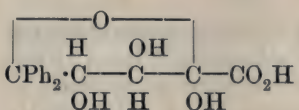
On benzoylation of diphenylarabitol, which is strongly dextrorotatory, an inactive tetrabenzoyl derivative is obtained,

$$HO{\cdot}CPh_2{\cdot}[CH(OBz)]_3{\cdot}CH_2{\cdot}O{\cdot}COPh.$$

Diphenylarabitol is converted on oxidation into benzophenone and aliphatic compounds, of which only mesotartaric acid could be isolated. Dilute nitric and other mineral acids eliminate water, forming anhydrodiphenyl-*l*-arabitol, $C_{17}H_{18}O_5$. This does not react with aldehyde or ketone reagents, and when oxidised with potassium permanganate yields an acid, $C_{17}H_{16}O_6$, without the elimination of the phenyl groups as benzophenone.



(I.)



(II.)

Accordingly, constitution (I), namely, 3 : 4-*dihydroxy*-2 : 2-*diphenyl*-5-*methyloltetrahydrofuran*, is assigned to the anhydro-compound, whilst the acid is 3 : 4 : 5-*trihydroxy*-2 : 2-*diphenyltetrahydrofuran*-5-*carboxylic acid* (constitution II).

On rearrangement this acid will form an α-ketonic acid,

$$OH{\cdot}CPh_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO{\cdot}CO_2H,$$

as witnessed by the formation of a dark red, oily hydrazone or osazone on treatment with phenyl hydrazine.

Triacetyl-l-*arabonolactone* forms large, transparent, well-formed, prismatic crystals with many faces, m. p. 52—54°, $[\alpha]_D^{18.5}$ $-60.45°$.

$\alpha\alpha$-*Diphenyl*-l-*arabitol* separates in small, colourless, flat needles, grouped concentrically, m. p. 171°, $[\alpha]_D^{20}$ $+85.6°$.

$\beta\gamma\delta\epsilon$-*Tetrabenzoyl*-$\alpha\alpha$-*diphenylarabitol* crystallises in colourless, silky, glistening needles, m. p. 181—182°, which are optically inactive.

Anhydrodiphenylarabitol crystallises in transparent, large, thin plates, m. p. 172—174°, $[\alpha]_D^{8}$ $-114.8°$.

3 : 4 : 5-*Trihydroxy*-2 : 2-*diphenyltetrahydrofuran*-5-*carboxylic acid* forms short, stunted needles, which sinter at 111°, m. p. 117°, $[\alpha]_D^{17}$ $+201.7°$.

$\alpha\alpha$-*Di*-p-*tolyl*-l-*arabitol* crystallises in small, glass-like, colourless, flat prisms with oblique end faces, in renniform aggregates. It has a faint aromatic odour, m. p. 186—187°, $[\alpha]_D^{18}$ $+71.62°$.

$\alpha\alpha$-*Dibenzyl*-l-*arabitol* forms transparent, colourless needles, m. p. 156—157°, $[\alpha]_D^{19}$ $+31.5°$.

E. F. A.

The Polymorphism of *allo*Cinnamic Acid. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1911, **17**, 976—984).—A more detailed account of results already published (compare Abstr., 1911, i, 975).

T. S. P.

Acylated Salicylic Acids. ALFRED EINHORN, LEO ROTHLAUF, and RUDOLF SEUFFERT (*Ber.*, 1911, **44**, 3309—3313).—Contrary to the experience of Lassar Cohn and Löwenstein (Abstr., 1908, i, 984), Einhorn and Seuffert find that benzoylsalicylic acid [*o*-benzoyloxybenzoic acid] may be readily prepared by the interaction of benzoyl chloride and salicylic acid in pyridine solution or by the action of benzoyl chloride on sodium salicylate. It crystallises in needles, m. p. 132°. The *sodium* salt was also analysed. The pyridine method was also found available for the preparation of *o-iso*valeryloxybenzoic acid, m. p. 95°, and of *o*-cinnamoyloxybenzoic acid, m. p. 150—152°.

Einhorn and Rothlauf have prepared o-*thymylcarbonatobenzoic acid*, $C_6H_3MePr\cdot O\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, m. p. 118°, by the action of thymolcarbonyl chloride on salicylic acid and dimethylaniline in benzene solution, and o-*menthylcarbonatobenzoic acid*,

$$C_6H_9MePr\cdot O\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

m. p. 121·5°, by mixing sodium salicylate and menthylcarbonyl chloride in acetone solution.

None of these compounds gives a coloration with ferric chloride.

H. W.

α-Chloro-β-phenyl-lactic Acid and Phenylacetaldehyde. BERTHOLD RASSOW and FRITZ BURMEISTER (*J. pr. Chem.*, 1911, [ii], **84**, 473—489).—By passing carbon dioxide into an aqueous solution of potassium hypochlorite and potassium cinnamate and subsequently acidifying, the authors obtain crystallised α-chloro-β-phenyl-lactic acid without a trace of oily by-product (compare Erlenmeyer and Lipp, Abstr., 1883, 992). The hydrated acid containing H_2O has m. p. 56—57°. By keeping over sulphuric acid, it changes to a labile, anhydrous acid, m. p. 86°, which in time is converted into a stable modification, m. p. 102—103°; the last is also obtained by repeatedly crystallising the hydrated acid from dry chloroform. The *ammonium* salt, m. p. 185° (decomp.), and the *aniline* salt, m. p. 82°, are described. Phenylacetaldehyde is best obtained by neutralising an aqueous solution of α-chloro-β-phenyl-lactic acid with sodium hydroxide and subsequently heating; it resinifies by keeping, and yields a crystalline *substance*, C_7H_7O, m. p. 148°. C. S.

The Anhydride of Mandelic Acid. KARL STUTZ (*Ber.*, 1911, **44**, 3485—3487. Compare Biedermann, Abstr., 1892, 473; Bischoff and Walden, Abstr., 1894, i, 525; Staudinger, Abstr., 1911, i, 308).—The vitreous amorphous anhydride of mandelic acid can also be obtained by heating the acid with a little sulphuric or hydrochloric acid in the steam-oven; obtained thus, it is soluble in ether, but insoluble in cold water and sodium hydrogen carbonate solution.

Although analysis and the equivalent weight indicate the formula $C_{32}H_{26}O_9$, the fact that the action of ammonia yields a larger quantity

of the amide than this formula would indicate leads the author to the opinion that either mandelic acid gives, like salicylic acid, several anhydrides, of which the vitreous substance is a mixture, or that the vitreous product represents the lactide, $C_8H_6O_2$, which, on account of its amorphous nature, has not yet been obtained free from water.

D. F. T.

Additive Products of Derivatives of Trinitrobenzene with Some Nitrogenous Aromatic Substances. ROBERTO CIUSA and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 377—383. Compare Abstr., 1911, i, 810; Sudborough and Beard, Trans., 1910, 97, 773; Ciusa and Agostinelli, Abstr., 1907, i, 553; Ciusa, Abstr., 1906, i, 962).—In addition to the additive products with picryl chloride formerly described, other compounds have now been prepared. Benzaldehyde-*p*-nitrophenylhydrazone and picryl chloride form a *compound*, $CHPh:N\cdot NH\cdot C_6H_4\cdot NO_2,2C_6H_2(NO_2)_3Cl$, which crystallises in carmine-red needles, m. p. 132°. The *compound* of benzaldehydephenylmethylhydrazone and picryl chloride,

$$CHPh:N\cdot NMePh,2C_6H_2(NO_2)_3Cl,$$

crystallises in dark red needles, m. p. 65°. The compound of cinnamaldehydephenylhydrazone and picryl chloride has m. p. 122—123° (formerly given incorrectly by printer's error). The *compound* of *m*-nitrobenzaldehydephenylhydrazone and picryl chloride,

$$NO_2\cdot C_6H_4\cdot CH:N\cdot NHPh,C_6H_2(NO_2)_3Cl,$$

forms dark red needles, m. p. 98°. The *compound* of piperonaldehydephenylmethylhydrazone and picryl chloride,

$$CH_2:O_2:C_6H_3\cdot CH\cdot N:NMePh,C_6H_2(NO_2)_3Cl,$$

crystallises in black needles with a violet lustre, and has m. p. 115°.

The *compound* of benzaldehydephenylhydrazone with trinitrotoluene, $CHPh:N\cdot NHPh,2C_6H_2Me(NO_2)_3$, forms dark red needles, m. p. 84°.

The *compound* of benzaldehydephenylhydrazone and trinitrophenol, $CHPh:N\cdot NHPh,2C_6H_2(NO_2)_3\cdot OH$, crystallises in violet-black needles, m. p. 117°.

The *compound* of *o*-nitrobenzaldehydephenylhydrazone with trinitrobenzene, $NO_2\cdot C_6H_4\cdot CH:N\cdot NHPh,C_6H_3(NO_2)_3$, crystallises in dark red needles, m. p. 132°.

The *compound* of benzaldehydephenyl-*p*-tolylhydrazone with trinitrobenzene, $CHPh\cdot N:NH\cdot C_6H_4\cdot Me,2C_6H_3(NO_2)_3$, forms lustrous, black scales, m. p. 142°.

The *compound* of cinnamaldehydephenylhydrazone and trinitrobenzene, $C_{15}H_{14}N_2,2C_6H_3(NO_2)_3$, crystallises in reddish-brown needles, m. p. 167°.

The *compound* of *m*-nitrobenzaldehydephenylhydrazone with trinitrobenzene, $NO_2\cdot C_6H_4\cdot CH:N\cdot NHPh,C_6H_3(NO_2)_3$, forms dark red needles, m. p. 136°.

The *compound* of *m*-nitrobenzaldehydephenylhydrazone and trinitrotoluene, $NO_2\cdot C_6H_4\cdot CH:N\cdot NHPh,C_6H_2(NO_2)_3Me$, crystallises in red needles, m. p. 105—106°.

The *compound* of *p*-nitrobenzaldehydephenylhydrazone and trinitrobenzene, $NO_2\cdot C_6H_4\cdot CH:N\cdot NHPh,C_6H_3(NO_2)_3$, forms dark red, lustrous scales, m. p. 144°.

The *compound* of anisaldehydephenylhydrazone with trinitrobenzene, $OMe\cdot C_6H_4\cdot CH{:}N\cdot NHPh,C_6H_3(NO_2)_3$, crystallises in reddish-brown scales, m. p. 113°.

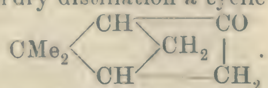
The *compound* of piperonaldehydephenylhydrazone and trinitrobenzene, $CH_2{:}O_2{:}C_6H_3\cdot CH{:}N\cdot NHPh,C_6H_3(NO_2)_3$, crystallises in almost black needles with a violet lustre, and has m. p. 147°.

The *compound* of benzaldehyde-*p*-nitrophenylhydrazone and trinitrobenzene, $CHPh{:}N\cdot NH\cdot C_6H_4\cdot NO_2,C_6H_3(NO_2)_3$, forms red needles, m. p. 164—165°.

Additive *compounds* of a very unstable kind were also obtained with trinitrophenol and benzaldehydephenylmethylhydrazone, piperonaldehydephenylmethylhydrazone, and *m*-nitrobenzaldehydephenylmethylhydrazone, as well as from *m*-nitrobenzaldehydemethylhydrazone and picryl chloride. R. V. S.

Derivatives of *cyclo*Pentanone. MARCEL GODCHOT and FELIX TABOURY (*Compt. rend.*, 1911, **153**, 1010—1011. Compare Abstr., 1911, i, 385).—The ketone prepared by the catalytic hydrogenation of *cyclo*pentanone is shown to be α-*cyclo*pentyl*cyclo*pentanone by the fact that on reduction, it gives α-cyclo*pentyl*cyclo*pentanol*, $C_5H_9\cdot C_5H_8\cdot OH$, needles, m. p. 20°, b. p. 125—126°/15 mm.; the *phenylurethane* has m. p. 88—89°. This substance has also been prepared by acting on *cyclo*pentanone with sodium ethoxide and reducing the resulting compound with alcohol and sodium (Wallach, Abstr., 1896, i, 572).
W. O. W.

Products of the Dry Distillation of Calcium Pinate. WALDEMAR BONSDORFF (*Ber.*, 1911, **44**, 3208—3210).—Calcium pinate was expected to yield on dry distillation a cyclic ketone,



The actual product was an oil, distilling between 50° and 100°/8 mm., which formed a semicarbazone, $C_9H_{15}ON_3$, crystallising in colourless plates, and yielded an unsaturated ketone on decomposition, probably 1-iso*propylene*-2-cyclo*pentanone*, $CMe_2{:}C<\begin{matrix}CO-CH_2\\ CH_2\cdot CH_2\end{matrix}$. This is a transparent oil, b. p. 69—71°/8 mm., D_4^{20} 0·9355, n_D 1·4666. E. F. A.

Fluorescence in the *p*-Benzoquinone Group. M. M. RICHTER (*Ber.*, 1911, **44**, 3469—3473).—When chloranil and potassium cyanide react in solution in methyl alcohol, there is formed the potassium salt of "cyananilic" acid, $C_8O_4N_2K_2$; the same substance is obtained when chloranilic acid is used instead of chloranil. These methods of preparation, together with the properties, show the free acid substance to be 2 : 5-*dicyano*-3 : 6-*dihydroxy*-p-*benzoquinone*. It is a brown solid, which does not crystallise well, and contains two firmly attached molecules of water of crystallisation; on heating, it carbonises without melting. It is a strong acid, and has a feeble quinone-like odour. Towards reducing and hydrolytic agents it is surprisingly stable. It is sparingly soluble in most solvents, but all the solutions show a strong fluorescence, the colour of which varies with the solvent. This fluorescence

(the first case with a *p*-benzoquinone derivative) leads the author to prefer the peroxide to the diketone structure for this compound (compare Kauffmann, Abstr., 1907, ii, 215). The *ammonium* salt, which exhibits a more beautiful fluorescence than the other salts, is precipitated from solution by concentrated ammonia solution as a dark brown, amorphous powder; the *silver* salt is also brown.

Monochloro-, 2 : 5-dichloro-, and trichloro-*p*-benzoquinone also react with potassium cyanide, yielding intensely fluorescent solutions; the product from the last-named is probably identical with cyananilic acid. D. F. T.

Phenanthrene Series. XXXII. Transition from the Phenanthraquinone to the Phenanthrene Series. JULIUS SCHMIDT and EBERHARD SAUER (*Ber.*, 1911, **44**, 3241—3255. Compare Abstr., 1911, i, 626).—When reduced with phosphorus and fuming hydriodic acid at 140°, 3-nitrophenanthraquinone yields two isomeric 3-*aminophenanthrene hydriodides*, of which the less soluble modification forms lustrous, rhombohedral crystals, m. p. 140°, whilst the more soluble isomeride, which forms the main product, crystallises in slender, white needles, m. p. 244—245°. Both isomerides on treatment with aqueous sodium hydroxide yield the same 3-aminophenanthrene, m. p. 87° (Werner, Abstr., 1902, i, 437).

2 : 9 : 10-*Trichlorophenanthrene*, prepared by heating phenanthraquinone with phosphorus pentachloride at 200°, crystallises in white needles, m. p. 144—145°, and on oxidation with chromium trioxide in aqueous acetic acid solution yields 2-*chlorophenanthraquinone*. This forms yellowish-red needles, m. p. 252—253°, and reacts with *o*-phenylenediamine hydrochloride in alcoholic solution, yielding 9-*chlorophenanthraphenazine*, $\begin{matrix} C_6H_3Cl\cdot C{:}N \\ | \qquad\quad | \\ C_6H_4 — C{:}N \end{matrix}\!\!>C_6H_4$, crystallising in white leaflets, m. p. 238°; the *oxime*, $C_{14}H_8O_2NCl$, m. p. 170—175°, and *semicarbazone*, $C_{15}H_{10}O_2N_3Cl$, slender, pale yellow needles, m. p. 220°, are described.

6-*Chloro-3-hydroxyphenanthratriazine*, $C_{12}H_7Cl\!<\!\begin{matrix} C{:}N\cdot CO \\ | \qquad | \\ C{:}N\cdot NH \end{matrix}$ or

$$C_{12}H_7Cl\!<\!\begin{matrix} C\cdot N\cdot C\cdot OH \\ | \qquad \| \\ C{:}N\cdot N \end{matrix},$$

prepared by the interaction of the preceding oxime and semicarbazide hydrochloride in alcoholic solution, has m. p. 288° (decomp.).

2-Chlorophenanthraquinone is oxidised by potassium dichromate and dilute sulphuric acid to 4-chlorodiphenic acid (Schmidt and Schall, Abstr., 1907 i, 26), which forms a *silver* salt, m. p. 270° (decomp.). When boiled with fuming nitric acid, it yields 2-*chlorodinitrophenanthraquinone*, $\begin{matrix} NO_2\cdot C_6H_2Cl\cdot CO \\ | \qquad\quad | \\ NO_2\cdot C_6H_3 — CO \end{matrix}$, which forms lustrous, yellow crystals, m. p. 274°, and is oxidised by potassium dichromate and sulphuric acid to 2-*chlorodinitrodiphenic acid*, $C_{14}H_7O_8N_2Cl$, m. p. 269°.

2-*Chlorodinitrophenanthraphenazine*, $\begin{matrix} NO_2\cdot C_6H_2Cl\cdot C{:}N \\ | \qquad\quad | \\ NO_2\cdot C_6H_3 — C{:}N \end{matrix}\!\!>C_6H_4$, prepared from 2-chlorodinitrophenanthraquinone and *o*-phenylenediamine

hydrochloride in alcoholic solution, forms a white, crystalline powder, m. p. 357°.

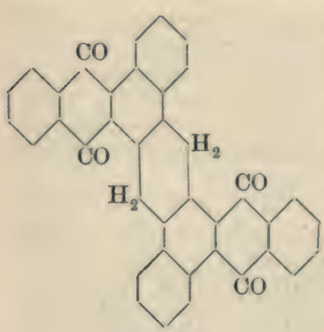
The interaction of 9 : 9-dichloro-10-phenanthrone (Schmidt and Lumpp, Abstr., 1909, i, 34) or 9-chloro-10-hydroxyphenanthrene and alcoholic potassium sulphide yields *di-9-hydroxy-10-phenanthryl sulphide*, $\left[C_6H_4 < {C_6H_4 - \atop C(OH)} > C\right]_2S$. This forms a light brown, crystalline powder, m. p. 223—224° (decomp.); the *dibenzoyl* derivative has m. p. 262—263°. F. B.

The Methyl-1 : 2-benzanthraquinone Group. I. ROLAND SCHOLL and WALTER TRITSCH (*Monatsh.*, 1911, **32**, 997—1018. Compare Bally and Scholl, Abstr., 1911, i, 676, 1097).—The authors have attempted with partial success to extend the anthraflavone and pyranthrone syntheses to the above group (compare Scholl, Abstr., 1910, i, 271).

2'-*Methyl-a naphthoylbenzoic acid* and the 4'-*methyl* isomeride were obtained by the action of phthalic anhydride and aluminium chloride on 2- and 1-methylnaphthalene respectively; the former product has m. p. 190—191°, and the latter 167—169°.

The latter substance (formula I), on reduction with zinc and acetic acid, yields the *lactone* of ω-hydroxy-ω-4'-*methyl-a-naphthyl*-o-*toluic acid*, m. p. 163—164°. On the other hand, reduction by sodium hydroxide and zinc dust gives ω-4'-*methyl-a-naphthyl*-o-*toluic acid*, a white, crystalline substance, m. p. 183—184°; the *ammonium* salt, unlike that of the parent ketonic acid, is easily soluble in water. The ammonium salt of the ketonic acid, when heated with strong sulphuric acid, condenses to 5-*methyl*-1 : 2-*benzanthraquinone* (formula II), consisting of yellow needles, m. p. 176—177°. By heating the last with alkali and a little anhydrous sodium acetate, simultaneous oxidation and condensation occur, with formation of 1 : 2 : 1' : 2'-*dibenzanthraflavone* (formula III); this gives orange-red crystals from nitrobenzene; with alkali and sodium hyposulphite it gives a vat which dyes unmordanted cotton yellow.

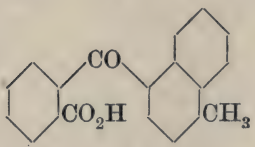
By careful nitration of 3-methyl-1 : 2-benzanthraquinone, there is obtained 1-*nitro*-5-*methyl*-1 : 2-*benzanthraquinone* in yellowish-brown crystals, m. p. 248—251°. Bromination produces 5-*bromomethyl*-1 : 2-*benzanthraquinone*, yellowish-green crystals, m. p. 219—221°, which by methyl-alcoholic potash is also condensed to dibenzanthraflavone (see above). Further bromination gives rise to a *pentabromo*-5-*methyl*-1 : 2-*dibenzanthraquinone*. Careful nitration of the monobromo-compound yields 1-*nitro*-5-*bromomethyl*-1 : 2-*benzanthraquinone*, m. p. 215—225° (decomp.).



(III.)

If 1-nitro-5-methyl-1 : 2-benzanthraquinone be reduced by phenylhydrazine there is formed 6-*hydroxy*-4-*methyl*-

dihydroindoloanthrene (formula IV); this substance, which is green, yields brown solutions. Air oxidises these solutions, giving a violet-brown precipitate of 4-*methylindoloanthrone*, which remains unmelted even at 360°. The last substance resembles benzoquinone in its behaviour as an oxidising agent, for example, towards phenylhydrazine and sulphurous acid. In certain aqueous solvents two molecules combine with one molecule of water to form a black *substance*, $C_{38}H_{24}O_3N_2$.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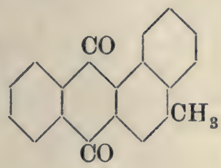
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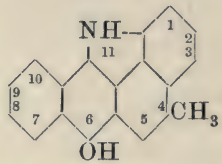

(IV.)

D. F. T.

Determination of Unsaturation in Hydroaromatic Substances. Isidor J. Klimont and Wilhelm Neumann (*Chem. Zentr.*, 1911, **82**, ii, 953; from *Pharm. Post*, **44**, 587—588).—A decigram of the terpene is dissolved in chloroform, and a known volume of an aqueous solution of potassium bromate (1 mol.) and potassium bromide (5 mols.) is added, followed by sulphuric acid (50%). Potassium iodide is added in known excess, and the iodine liberated is titrated. T. A. H.

Catalytic Reactions at High Pressures and Temperatures. XXIV. Hydrogenation of the Terpenes. Wladimir Ipatieff and G. Balatschinsky (*Ber.*, 1911, **44**, 3461—3466).—The experiments were carried out with nickel oxide as catalyst, the initial pressure of the hydrogen being 100—130 atmospheres.

In the hydrogenation of the terpene ketones the double linkings add on hydrogen at 220—240°, irrespective of whether they are situated in the nucleus or in the side-chain. The reduction of the carbonyl group takes place at 260—280°; in the menthol series the temperature must not exceed 260°, otherwise menthane is formed. The optical rotation of the compounds produced is all the greater the lower the temperature of hydrogenation.

The above conclusions are drawn from the following experiments: at 280°, carvone gives carvomenthol, from which a mixture of two menthenes was obtained by loss of water in the pressure apparatus at 365°, with alumina as the catalyst. At 220° and 240°, carvomenthone was formed from carvone, the specific rotation of the product being greater at 220° than at 240°. At 280° pulegone gives menthane, but at 220—240° menthone is produced. At 250°, menthone gives menthol on prolonged hydrogenisation. Thymol gives *i*-menthol at 260°, m. p. 9°, D_{20} 0·8970, n_D 1·45659. T. S. P.

Action of Nitrosyl Chloride on the Essential Oil of Bupleurum fructicosum. Nitroso-chlorides. Derivatives and Decomposition Products. Dihydrocuminaldehyde. III. Luigi Francesconi and E. Sernagiotto (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 388—392. Compare Abstr., 1911, i, 1000).—When the nitroso-

chloride previously described is warmed with 25% acetic acid a vigorous decomposition occurs, accompanied by the evolution of gas, chiefly hydrogen chloride. When the product is distilled with steam the non-volatile portion is a nitrogenous *substance*, m. p. 68°. The part volatile with steam is an oil, a portion of which readily yields a bisulphite compound, and behaves in other respects as an aldehyde. On oxidation with silver oxide, it yields cuminic acid, and is regarded by the authors as a *dihydrocuminaldehyde*. It has the formula $C_{10}H_{14}O$, b. p. 136—140°/15 mm., D^{13} 0·9825, n_D 1·5280—1·5305, and is dextrorotatory. The *semicarbazone* crystallises in silvery laminæ, m. p. 197—198°. The *aldazine*, $(C_{10}H_{14}N)_2$, forms yellow plates, m. p. 111—112°. The *phenylhydrazone*, $C_{16}H_{20}N_2$, has m. p. 123—126°. The p-*bromophenylhydrazone*, $C_{16}H_{19}N_2Br$, crystallises in pale yellow laminæ, m. p. 127—129°. The semicarbazone and especially the two hydrazones are phototropic, and all the compounds mentioned are dextrorotatory. R. V. S.

Essential Oil of Litsea odorifera Leaves. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 325—327).—The oil, known as "trawas oil" in Java, has D^{15} 0·836—0·846, α_D −10′ to −7° in a 20 cm. tube, and boils mostly at 120—125°/10 mm. pressure or at 233°/760 mm.; it is pale yellow and possesses a disagreeable odour.

The oil contains *l*-methyl-*n*-nonylcarbinol, α_D −5°40′ (compare Power and Lees, Trans., 1902, **81**, 1593), l-*undecenyl alcohol*,

$$CH_2{:}CH{\cdot}[CH_2]_7{\cdot}CHMe{\cdot}OH,$$

D^{10} 0·835, b. p. 233°, α_D −5°10′, and *undecenone*, $CH_2{:}CH{\cdot}[CH_2]_7{\cdot}COMe$, m. p. −7°, b. p. 235°, $D^{11\cdot5}$ 0·848, MR = 52·47 (calc. for $C_{11}H_{20}O$ = 52·51), which yields a *semicarbazone*, m. p. 116°, and a *dibromide*, b. p. 204°/15 mm. From the latter the unsaturated ketone can be recovered by treatment with zinc dust and alcohol. T. A. H.

Essential Oil of Santolina chamæcyparissus. III. Formula of Santolinenone, $C_{10}H_{16}O$. LUIGI FRANCESCONI and P. SCARAFÌA (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 383—387. Compare Abstr., 1911, i, 1001).—The authors discuss the constitution of the ketone, $C_{10}H_{16}O$, obtained from this essential oil, and assign to it the formula of $\Delta^{1:7}$-menthene-2-one. R. V. S.

Fresh Dammar Resin from Central Borneo. EM. GOTTLIEB (*Arch. Pharm.*, 1911, **249**, 701—705).—This variety of dammar is known in Borneo as "Dammar Daging," and is possibly derived from *Retinodendron Rassak*. The figures in brackets give the percentage of the material dissolved by the solvents named: alcohol (82), methyl alcohol (70), acetone (60), chloroform (18). The resin had the following constants: acid number, direct, 140·0—142·0, indirect, 148·4—151·2; saponification value, cold, 159·6—162·4, hot, 163·5—165·2.

The portion soluble in ether yielded in turn to (*a*) sodium carbonate solution (1%), *dagingolic acid*, $C_{24}H_{44}O_4$, m. p. 170°, and (*b*) potassium hydroxide solution (1%), *digingolic acid*, $C_{13}H_{26}O_3$, m. p. 125—126°. The residue, freed from ether, yielded on steam distillation an essential oil and *dagingoresen*, $C_{22}H_{28}O$. The two acids and the resen give phytosterol-like colour reactions with the usual reagents. T. A. H.

Recent Fossil Dammar Resin from Central Borneo. EM. GOTTLIEB (*Arch. Pharm.*, 1911, **249**, 705—710).—The following figures give the percentage solubilities of the resin in the solvents named: ether (65), acetone (40), turpentine oil (35), alcohol (28).

The portion soluble in ether yielded to (*a*) ammonium carbonate solution (1%), a resin *acid*, $C_{16}H_{26}O_2$, m. p. 135°, (*b*) sodium carbonate solution (1%), a resin *acid*, $C_{14}H_{32}O_2$, m. p. 103—105°, (*c*) potassium hydroxide solution (1%), a resin *acid*, $C_{12}H_{18}O_2$, m. p. 120—122°, and the residue on steam distillation furnished essential oil and an impure *resen*.

The portion insoluble in ether was dissolved, in part, on further addition of alcohol, and from this, by means of potassium hydroxide solution, a *substance*, $C_{12}H_{22}O$, was obtained, leaving a *resen*, $C_{12}H_{22}O_2$. The three acids and the resene all gave phytosterol-like colour reactions. The resin contained a bassorin-like substance. T. A. H.

Decomposition of Gynocardin by the Enzyme of the Leaves of Pangium edule. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1911, **30**, 220—221).—Gynocardin is decomposed at the ordinary temperature by the enzyme, giving dextrose and a *compound*, $C_6H_8O_4$, according to the equation: $C_{13}H_{19}O_9N + H_2O = C_6H_{12}O_6 + HCN + C_6H_8O_4$. This substance, $C_6H_8O_4$, is a diketone, and yields a *phenylhydrazone*, which decomposes at 177°.

If the fermentation takes place in a closed vessel, and the quantities of hydrogen cyanide and the diketone formed are estimated from time to time, the yields are a maximum after four hours, and then they diminish proportionately. The specific rotatory power also diminishes with the duration of the reaction. W. G.

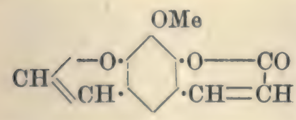
Saponins. ERNST WINTERSTEIN and H. BLAU (*Zeitsch. physiol. Chem.*, 1911, **75**, 410—442).—Saponin prepared from *Sapindus utilis* forms, on hydrolysis with sulphuric acid, lævulose, arabinose, and rhamnose; dextrose and galactose do not appear to be formed. Lævulose is split off by dilute mineral acids at low temperatures, and also a small quantity of an amorphous product which, by the action of stronger acids at higher temperatures, produces arabinose and rhamnose. This amorphous substance, "pentoside," still belongs to the group of the glucosides, and differs from saponin by being insoluble in water, and its great solubility in alcohol. Its decomposition by strong acids into arabinose and rhamnose is accompanied by the formation of a crystalline compound, to which the formula $C_{18}H_{28}O_3$ has been given. This is the true sapogenin; it gives, on distillation

with zinc dust, higher hydrocarbons, and also a gas which consists partly of butylene.

Sapogenin forms a monomethyl and monoacetyl compound. By acetylation saponin is greatly affected in its chemical constitution and physiological action.

Saponin from horse chestnut gives, on hydrolysis, sapogenin, arabinose, dextrose, and lævulose. H. B. H.

The Constitution of Xanthotoxin and its Relationship to Bergaptene. HERMANN THOMS [with HANS PREIS] (*Ber.*, 1911, **44**, 3325—3332).—Two crystalline substances have been isolated from the residue left after the steam distillation of the fruit of *Fagara Xanthoxyloides.* One of these, m. p. 190—191°, has been shown to be identical with bergapten obtained from oil of bergamot. The second substance, *xanthotoxin*, $C_{12}H_8O_4$, has m. p. 145—146°. On nitration in acetic acid solution, xanthotoxin yields *nitroxanthotoxin*, $C_{12}H_7O_6N$, m. p. 233°, whilst, when treated with methyl iodide in methyl-alcoholic alkaline solution, it becomes transformed into *methylxanthotoxic acid*, $C_{12}H_{11}O_3 \cdot CO_2H$, m. p. 114—117°, and *methyl methylxanthotoxate*, m. p. 44°. When fused with potassium hydroxide, xanthotoxin yields pyrogallolcarboxylic acid. From these experiments the annexed formula is proposed. A pharmacological comparison of the effect of xanthotoxin and bergapten on fishes shows the former to be the more powerful poison. H. W.



Chlorophyll. XVII. Absorption Spectra of the Components and of the Primary Derivatives of Chlorophyll. RICHARD WILLSTÄTTER, ARTHUR STOLL, and MAX UTZINGER (*Annalen*, 1911, **385**, 156—188).—The absorption spectra of the following substances in ether (0·03—0·04 gram per litre) have been measured: chlorophyll *a* and *b*, methylchlorophyllide *a* and *b*, phæophytin *a* and *b*, methylphæophorbide *a* and *b*, phytochlorin *e* and *f*, and phytorhodin *g*. The authors find that chemical methods are more sensitive than spectrum analysis for the examination of chlorophyll derivatives; thus the presence of a little chlorophyll *a* in chlorophyll *b*, or vice versa, cannot be detected by the spectrometer, neither are the changes through which chlorophyll passes in its conversion into the feebly basic products of hydrolysis betrayed by the absorption spectra; phytochlorin *e* and *f* show almost identical spectra in spite of their great chemical dissimilarity.

The absorption spectra of chlorophyll *a* and *b* respectively exhibit very slight differences from those of the methylchlorophyllides *a* and *b*. The same is true for the magnesium-free derivatives of the four substances, namely, the phæophytins *a* and *b* and the methylphæophorbides *a* and *b*. Willstätter and Benz's crystallised chlorophyll (Abstr., 1908, i, 199) is a mixture of ethylchlorophyllides *a* and *b*, rich in the former.

The absorption bands in the spectrum of phytochlorin *e* show, in intensity, breadth, and position, a remarkable similarity to those in

the spectrum of phæophytin *a*; also the comparatively simple spectrum of phytorhodin *g* is nearly related to the far more complicated spectrum of phæophytin *b*, or of methylphæophorbide *b*. These similarities are very remarkable when the differences in the compositions of the substances are considered. The absorption spectra of phytochlorin *e*, phytorhodin *g*, and *iso*chlorophyllins *a* and *b* (Abstr., 1911, i, 659) in dilute methyl-alcoholic potassium hydroxide are described, and the constitutions of chlorophyll derivatives containing potassium, zinc, iron, or copper in place of the magnesium of the natural product are discussed. C. S.

Chlorophyll. XVIII. Reduction of Chlorophyll. RICHARD WILLSTÄTTER and YASUHIKO ASAHINA (*Annalen*, 1911, **385**, 188—225).—Malarski and Marchlewski have shown that chlorophyll-pyrrole and hæmopyrrole yield identical azo-compounds with diazonium salts (Abstr., 1910, i, 692). With the primary object of comparing these two pyrroles, the authors have reduced (i) hæmin by hydriodic acid, D 1·96, and phosphonium iodide by a modification of Nencki and Zaleski's method, (ii) hæmatoporphyrin by Piloty's method (Abstr., 1909, i, 539), and (iii) various chlorophyll derivatives (phytochlorins, phytorhodins, ethylchlorophyllides *a* and *b*, but best of all, phylloporphyrin) by both methods. In each case the reduction products are basified by sodium carbonate and distilled with steam, and the ethereal extract of the bases is freed quantitatively from pyrrolines and pyrrolidines by sodium dihydrogen phosphate, and is finally separated into three substances, hæmopyrrole, *iso*hæmopyrrole, and phyllopyrrole, by fractional salt-formation with ethereal picric acid (compare this vol. i, 50, 56).

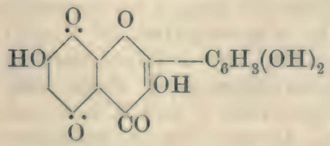
Haemopyrrole, $NH<\begin{matrix}CMe:CEt\\ CH=CMe\end{matrix}$, b. p. 198°/730 mm. or 86—87°/12 mm., D_4^0 0·930, and D_4^{20} 0·918, which resembles most closely the "hæmopyrrole" of the literature, is a colourless liquid, which resinifies rapidly in the air, and responds to the pine-shaving and to Ehrlich's dimethylaminobenzaldehyde tests for pyrroles; it forms a *picrate*, m. p. 111° (corr.), *chloropicrate*, m. p. 123° (decomp.), and *styphnate*, $C_8H_{13}N,C_6H_3O_8N_3$, m. p. 120—121° (decomp.) (styphnic acid forms with pyrroles salts which are better suited than the picrolonates for the identification of the bases, on account of their stability, sparing solubility, and crystallisability), and reacts with nitrous acid to form an *oxime*, m. p. 201°, of methylethylmaleinimide.

iso*Haemopyrrole*, $NH<\begin{matrix}CMe:CMe\\ CH=CEt\end{matrix}$, m. p. 16—17°, b. p. 198°/725 mm. or 88°/11—12 mm., D_4^{20} 0·915, is a colourless liquid with a characteristic odour. It exhibits the colour reactions of pyrroles, reddens and resinifies in the air, and forms a *picrate*, m. p. 119°, *chloropicrate*, m. p. 126°, and *styphnate*, m. p. 136°, decomp. 140°. With nitrous acid it forms an *oxime*, m. p. 221—222° (corr.), of methylethylmaleinimide. It is reduced by hydriodic acid and phosphorus at 240° to a mixture of the pyrroline and the pyrrolidine, which is completely reduced by hydrogen and platinum to iso*haemo*-

pyrrolidine, $C_8H_{17}N$, b. p. 155—156°/730 mm., D_4^0 0·845, D_4^{20} 0·830 (*platinichloride*, m. p. 191—192°; *a-naphthylcarbamide*, m. p. 138°).

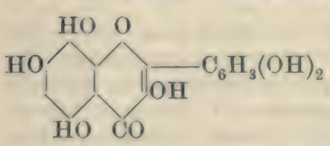
Phyllopyrrole, $NH<\begin{matrix}CMe\!:\!CMe\\ CMe\!:\!CEt\end{matrix}$, m. p. 63°, b. p. 213°/725 mm. or 92—93°/12 mm. (m. p. 66—67°, b. p. 88—90°/10 mm., when obtained from chlorophyll derivatives), white leaflets, resinifies rapidly in the air, and does not react with a pine-shaving or dimethylaminobenzaldehyde or with mercuric chloride. It forms a *picrate*, m. p. 95°, and yields by reduction (as above) *phyllopyrrolidine*, $C_9H_{17}N$, b. p. 160—164°, D_4^{20} 0·824 (*a-naphthylcarbamide*, m. p. 145°). C. S.

Anthocyanins. I. An Anthocyanin-like Oxidation Product of Quercitin. MAXIMILIAN NIERENSTEIN and MURIEL WHELDALE (*Ber.*, 1911, **44**, 3487—3491. Compare this vol., ii, 80).—The red, violet and blue colouring matters of flowers are regarded as oxidation products of the tannins; they are also related to the yellow plant dyes. On oxidation of quercetin with chromic acid in acetic acid solution, *quercetone* (annexed formula), crystallising in small, deep red needles, m. p. above 360°, is obtained. Like anthocyanin, it dissolves in alkali hydroxides with a blue, and in concentrated sulphuric acid with a red, coloration.



It could not be methylated or acetylated; the *tetrabenzoylquercetone*, prepared by the action of benzoyl chloride on quercetone dissolved in a mixture of quinoline and pyridine, crystallises in small, pointed needles, m. p. 281—283°. On fusion of quercetone with alkali, protocatechuic acid was obtained.

When heated with acetic anhydride and zinc dust, acetylated *hydroxyquercetin* is obtained as a colourless, amorphous powder, yielding on hydrolysis 1 : 3 : 4 : 3′ : 4′-*pentahydroxyflavonol* (annexed formula). This crystallises in small, yellow, microscopic needles, which lose a molecule of water at 160°, m. p. 352—355°. Both alkali hydroxides and sulphuric acid dissolve it with a yellow coloration. 1 : 3 : 4 : 3′ : 4′-*Pentamethoxyflavonol* forms small, colourless needles, which sinter at 136—138°, m. p. 147—149°. It is probably converted into veratric acid when heated with alcoholic potassium hydroxide at 170°. E. F. A.



Melanins. MAURICE PIETTRE (*Compt. rend.*, 1911, **153**, 1037—1040. Compare Abstr., 1911, ii, 1006).—The melanin from *Sepia officinalis* on hydrolysis with sulphuric acid gives tyrosine, leucine, amorphous amino-acids, and an insoluble pigment. After alkali hydrolysis, alanine and amorphous amino-acids are obtained, together with a pigment which is readily soluble in alkalis. Artificial melanin, prepared by the action of *Russula* extract on tyrosine, gave no tyrosine on hydrolysis; leucine, however, was recognised amongst the products. The two melanins, therefore, resemble those already

examined, in containing a protein group united to a pigment. The name *melainin* is suggested for the latter substance. W. O. W.

The Composition of Tannin. LEO F. ILJIN (*Ber.*, 1911, **44**, 3318—3319).—The author points out that the hygroscopic nature of tannin may account for the differences in the analytical results obtained by him and by Steinkopf and Sargarian (Abstr., 1911, i, 1004). He quotes an experiment which shows the great readiness with which moisture is absorbed by tannin. H. W.

Carboxonium Compounds. FRIEDRICH KEHRMANN and JOSEPH KNOP (*Ber.*, 1911, **44**, 3505—3513).—The reaction between ethereal magnesium phenyl bromide and 3 : 6-dimethylxanthone in benzene leads ultimately to the formation of 9-*phenyl*-3 : 6-*dimethylxanth-hydrol*, $C_6H_3Me<\genfrac{}{}{0pt}{}{CPh(OH)}{O}>C_6H_3Me$, m. p. 152° (corr.). The fact that this substance forms an anhydrous, blackish-green, crystalline *iodide*, $C_{21}H_{17}OI$ (and also the corresponding *bromide* and *chloride*), which is remarkably stable in the presence of water, is regarded as additional evidence that such coloured halides are oxonium salts, not quinonoid carbonium salts, as stated by Gomberg and Cone (Abstr., 1910, i, 55). Still more stable is the *chloride* of *methyl* 9-*phenyl*-3 : 6-*dimethylxanthonium*-o-*carboxylate*, $CO_2Me\cdot C_6H_4\cdot C<\genfrac{}{}{0pt}{}{C_6H_3Me}{C_6H_3Me}>O\cdot Cl$, orange-yellow needles, which is prepared by saturating a cold methyl-alcoholic solution of 3 : 6 dimethylfluoran with hydrogen chloride; the corresponding *bromide*, *iodide*, and *platinichloride* are described, as also are the *chloride*, *bromide*, and *platinichloride* of the corresponding *ethyl* ester.

9-*Phenyl*-2 : 7-*dimethylxanth-hydrol*, obtained by the oxidation of 9-phenyl-2 : 7-dimethylxanthene, forms oxonium salts, which are redder than those of the preceding isomeride, and are completely hydrolysed by water; the *ferrichloride*, $C_{21}H_{17}OCl,FeCl_3$, crystallises in orange-red prisms. C. S.

Studies in the Coumarone Group. JOSEF TAMBOR [with S. GÜNSBURG, O. KELLER, CHANSCHY-HERZENBERG, B. ROSENKNOPF, and J. LICHENTENBAUM] (*Ber.*, 1911, **44**, 3215—3223).—Alkyl ethers of 1-hydroxybenzoylcoumarone are obtained (1) by the action of alcoholic potassium hydroxide on *o*-acetoxychalkone dibromides; (2) by the interaction of coumarilyl chloride with phenol ethers and aluminium chloride (Zwayer and Kostanecki, Abstr., 1908, i, 443), and (3) by the condensation of salicylaldehyde with α-bromoacetophenone in alcoholic alkaline solution. A number of substituted 1-benzoylcoumarone derivatives have been prepared by these methods.

2-*Hydroxy*-2′ : 5′-*dimethoxychalkone*,

$$OH\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot C_6H_3(OMe)_2,$$

from quinacetophenone dimethyl ether and salicylaldehyde, crystallises in orange prisms, m. p. 119·5°. Neither the acetate nor the dibromide is crystalline.

2′ : 5′-*Dimethoxy*-1-*benzoylcoumarone*,

$$C_6H_4 \lessdot \genfrac{}{}{0pt}{}{-O-}{CH} \gtrdot C \cdot CO \cdot C_6H_3(OMe)_2,$$

crystallises in yellow plates, m. p. 98°, which when moistened with concentrated sulphuric acid become dark red, and give an orange solution. The *phenylhydrazone* crystallises in slender needles, m. p. 161°.

a-Bromo-3 : 5-*dimethoxyacetophenone*, $C_6H_3(OMe)_2 \cdot CO \cdot CH_2Br$, from quinol dimethyl ether, bromoacetyl bromide, and aluminium chloride, crystallises in colourless needles, m. p. 91°. It condenses with salicylic aldehyde to form dimethoxybenzoylcoumarone.

2′ : 4′-*Diethoxy*-1-*benzoylcoumarone*, from resorcinol diethyl ether and coumarilyl chloride, crystallises in almost colourless prisms, m. p. 87°. The crystals are coloured orange by concentrated sulphuric acid.

2-*Hydroxy*-2′ : 4′-*diethoxychalkone* crystallises from dilute alcohol in greenish-yellow prisms, and from concentrated alcohol in sulphur-yellow needles, m. p. 164° (decomp. and green coloration) in each case. With concentrated sulphuric acid, the crystals become yellow.

2-*Acetoxy*-2′ : 4′-*diethoxychalkone* forms small, colourless needles, m. p. 69°.

2-*Hydroxybenzylidene-bis*-2′ : 4′-*diethoxyacetophenone*,

$$HO \cdot C_6H_4 \cdot CH[CH_2 \cdot CO \cdot C_6H_3(OEt)_2]_2,$$

from salicylaldehyde and resacetophenone diethyl ether, separates in greenish-yellow needles, m. p. 75°.

On bromination of 2-acetoxydiethoxychalkone, 2-*acetoxy*-2′ : 4′-*diethoxy*-5′-*bromochalkone dibromide* is obtained in colourless prisms, m. p. 139°.

5′-*Bromo*-2′ : 4′-*diethoxy*-1-*benzoylcoumarone*, obtained by the action of potassium hydroxide on the foregoing and also on brominating diethoxybenzoylcoumarone, crystallises in colourless prisms, m. p. 143°.

Resacetophenone diethyl ether and 5-bromosalicylaldehyde condense to form 5-*bromo*-2-*hydroxy*-2′ : 4′-*diethoxychalkone*,

$$OH \cdot C_6H_3Br \cdot CH \colon CH \cdot CO \cdot C_6H_3(OEt)_2,$$

which crystallises in lustrous, yellow needles, m. p. 175° (decomp.). The *acetyl* derivative forms lustrous, light yellow needles, m. p. 112°.

5-*Bromo*-2-*acetoxy*-2′ : 4′-*diethoxychalkone dibromide* gives colourless, rhombohedric crystals, m. p. 147°.

5-*Bromo*-2′ : 4′-*diethoxy*-1-*benzoylcoumarone* forms colourless, rhombohedric crystals, m. p. 126°, which are coloured red by concentrated sulphuric acid; the compound is totally different from the isomeric 5′-bromo-derivative just described.

5-*Methoxy*-2 : 3-*dimethylcoumarilyl chloride* forms faintly green-coloured needles, m. p. 137°.

Condensed with anisole and aluminium chloride, 5 : 4′-*dimethoxy*-1-*benzoyl*-2 : 3-*dimethylcoumarone*,

$$OMe \cdot C_6H_2Me \lessdot \genfrac{}{}{0pt}{}{-O-}{CMe} \gtrdot C \cdot CO \cdot C_6H_4 \cdot OMe,$$

yields lustrous, colourless needles, m. p. 145°.

5 : 3′ : 4′-*Trimethoxy*-1-*benzoyl*-2 : 3-*dimethylcoumarone* forms lustrous, colourless needles, m. p. 156°.

5 : 2′ : 4′-*Trimethoxy*-1-*benzoyl*-2 : 3-*dimethylcoumarone* crystallises in yellow needles, m. p. 115°.

5 : 2′ : 5′-*Trimethoxy*-1-*benzoyl*-2 : 3-*dimethylcoumarone* separates in yellow cubes, m. p. 135°.

5 : 2′ : 4′ : 6′-*Tetramethoxy*-1-*benzoyl*-2 : 3-*dimethylcoumarone* crystallises in well-formed, yellow, prismatic columns, m. p. 196—197°.

5 : 2′ : 3′ : 4′-*Tetramethoxy*-1-*benzoyl*-2 : 3-*dimethoxycoumarone* forms slender, yellow needles, m. p. 158°.

5-*Methoxy*-2-*methylcoumarilic chloride* forms green needles, m. p. 104—105°. It has been condensed with phenol methyl ethers to form the following compounds :

5 : 4′-*Dimethoxy*-1-*benzoyl*-2-*methylcoumarone* forms pale yellow platelets, m. p. 140°.

5 : 3′ : 4′-*Trimethoxy*-1-*benzoyl*-2-*methylcoumarone* crystallises in small, colourless platelets, m. p. 153—154°.

5 : 2′ : 4′ : 6′-*Tetramethoxy*-1-*benzoyl*-2-*methylcoumarone* crystallises in dark yellow, microscopic plates, m. p. 178°.

5 : 2′ : 3′ : 4′-*Tetramethoxy*-1-*benzoyl*-2-*methylcoumarone* forms pale yellow, clearly-defined needles, m. p. 72—73°.

These compounds are all coloured red by concentrated sulphuric acid. E. F. A.

Interaction of Homologous Phenols with Methylcoumaric Acid Dibromide. II. Richard Stoermer and C. Friemel (*Ber.*, 1911, **44**, 3256—3266).—In continuation of previous work (Abstr., 1911, i, 632), the authors have studied the interaction of methylcoumaric (*o*-methoxycinnamic) acid dibromide and *m*-cresol. When equal parts of these substances are heated for ten minutes on the water-bath, the following products are obtained : (1) *β*-o-*methoxyphenyl*-*αβ*-*di*-p-*hydroxy*-o-*tolylpropionic acid*,

$$\mathrm{OMe{\cdot}C_6H_4{\cdot}CH(C_6H_3Me{\cdot}OH){\cdot}CH(C_6H_3Me{\cdot}OH){\cdot}CO_2H},$$

which crystallises from dilute acetone in colourless needles, m. p. 274°, and yields a *methyl* ester, crystallising in small columns, m. p. 225° ; the *di*-p-*nitrobenzoyl* derivative, $C_{39}H_{32}O_{11}N_2$, forms light yellow, rhombic plates, m. p. 216°. (2) 4-o-*Methoxyphenyl*-7-*methylcoumarin*,

$$\begin{array}{l} \mathrm{CMe{:}CH{\cdot}C{-\!\!-\!\!-}O{-\!\!-\!\!-}CO} \\ \mathrm{CH{=}CH{\cdot}C{\cdot}C(C_6H_4{\cdot}OMe){:}CH} \end{array},$$

which crystallises from glacial acetic acid in rhombic columns, m. p. 220°, and is also obtained by the removal of hydrogen bromide from the compound (3) described below by means of quinoline. (3) 3-*Bromo*-4-o-*methoxyphenyl*-7-*methylhydrocoumarin*,

$$\begin{array}{l} \mathrm{CMe{:}CH{\cdot}C{-\!\!-\!\!-}O{-\!\!-\!\!-}CO} \\ \mathrm{CH{=}CH{\cdot}C{\cdot}CH(C_6H_4{\cdot}OMe){\cdot}CHBr} \end{array},$$

which crystallises in rectangular plates, m. p. 123°, and, when heated with strong aqueous sodium hydroxide, loses hydrogen bromide, yielding 2-o-*methoxyphenyl*-5-*methylcoumaran*-1-*carboxylic acid*,

$$\begin{array}{l} \mathrm{CMe{:}CH{\cdot}C{\cdot}O{\cdot}CH{\cdot}CO_2H} \\ \mathrm{CH{=}CH{\cdot}C{-\!\!-}CH{\cdot}C_6H_4{\cdot}OMe} \end{array}.$$

This crystallises in rhombic platelets, m. p. 199°, having a pale blue fluorescence, and yields a sparingly soluble, yellow *sodium* salt ; the *piperidide*, $C_{22}H_{25}O_3N$, forms slender, colourless columns, m. p.

148—149°; the *methyl* ester crystallises in hexagonal plates, m. p. 75°. The *hydrazide*, prepared by heating the methyl ester with hydrazine hydrate in alcoholic solution, has m. p. 110°, and yields the corresponding *azoimide* when treated with sodium nitrite in aqueous acetic acid solution.

1-*Carbethoxyamino*-2-o-*methoxyphenyl*-5-*methylcoumaran*,

$$C_6H_3Me\left\langle\begin{array}{l}O\cdot CH\cdot NH\cdot CO_2Et\\ \quad\;\; | \\ \!\!-\!\!-CH\cdot C_6H_4\cdot OMe\end{array}\right.,$$

obtained by boiling an alcoholic solution of the azoimide, crystallises in very thin, colourless leaflets, m. p. 143—144°, and is converted on heating with concentrated hydrochloric acid and alcohol into 2-o-*methoxyphenyl*-5-*methylcoumarone*, $C_6H_3Me\left\langle\begin{array}{c}\text{———}O\text{———}\\ C(C_6H_4\cdot OMe)\end{array}\right\rangle CH$, which is an oil, b. p. 220—223°/25 mm., gives an intense orange-red coloration with sulphuric acid, and, on reduction with sodium in alcoholic solution, yields 2-o-*methoxyphenyl*-5-*methylcoumaran*,

$$C_6H_3Me\left\langle\begin{array}{c}\text{———}O\text{———}\\ CH(C_6H_4\cdot OMe)\end{array}\right\rangle CH_2.$$

This crystallises from alcohol in lustrous, silky needles, having a pale blue fluorescence, m. p. 96—97°.

The constitution of the two last-mentioned compounds has been established by their synthesis from *o*-methoxymandelonitrile and *m*-cresol. When heated with sulphuric acid, these condense to form the *lactone* of o-*methoxyphenyl*-o-*hydroxy*-p-*tolylacetic acid*,

$$\begin{array}{l}CMe\!:\!CH\cdot CH\cdot O\cdot CO\\ |\qquad\quad\;\; \| \qquad\quad |\\ CH\!=\!CH\cdot CH\text{——}C\cdot C_6H_4\cdot OMe\end{array},$$

which has m. p. 116—119°, and is converted into 2-*o*-methoxyphenyl-5-methylcoumarone by heating with phosphorus pentasulphide.

F. B.

Corydalis Alkaloids. XI. Corytuberine. JOHANNES GADAMER (*Arch. Pharm.*, 1911, **249**, 641—669. Compare Dobbie and Lauder, Trans., 1893, **63**, 485; Gadamer and Wagner, Abstr., 1902, i, 391; Schmidt, Abstr., 1909, ii, 85, and Gadamer, Abstr., 1911, i, 1011, 1012).—A general discussion of the constitutions and relationships of the corytuberine group of alkaloids has been given already (Abstr., 1911, i, 1011), and in the present paper the experimental data on which the formula then assigned to corytuberine was based are given.

The alkaloid is best obtained by distilling the alcohol from an alcoholic extract of *Corydalis* roots, dissolving the residue in water, so that the aqueous mixture weighs twice as much as the weight of roots used, filtering, adding ammonia solution in very slight excess to the filtrate, shaking rapidly with ether, and removing the separated aqueous layer as quickly as possible. The aqueous liquid so treated continues to deposit impure crystals of corytuberine for several days. This may be purified by fractional precipitation by ammonia solution from the hydrochloride, washing with water, alcohol, and ether in turn, and finally recrystallising from boiling water. The alkaloid has the formula $C_{19}H_{21}O_4N,5H_2O$ (compare *loc. cit.*).

With benzoyl chloride, by the Schotten-Baumann method, it furnishes a crystalline *monobenzoyl* derivative, m. p. 211—214°, $[\alpha]_D^{20}$ +151·5° in chloroform, and a *dibenzoyl* derivative, m. p. 135—140°, $[\alpha]_D^{20}$ +128·8—133·5° in chloroform, which is amorphous, but yields a crystalline *hydrochloride*. On boiling with benzoyl chloride a *tribenzoyl* (possibly tetrabenzoyl) derivative, m. p. 140—142° (approx.), $[\alpha]_D^{20}=0°$, crystallising in glandular masses of crystals, is formed.

On methylation with methyl sulphate by Pschorr and Karo's method (Abstr., 1906, i, 878), a mixture of two methylcorytuberine methosulphates with some corytuberine methosulphate is produced. With diazomethane a mixture of two methylcorytuberines with two methylcorytuberine methylhydroxides is formed. One of the methylcorytuberines is identical with corydine (see following abstract), and the other has been named *iso*corydine (*loc. cit.*). When diazomethane is generated in presence of corytuberine suspended in *iso*amyl ether, *dimethylcorytuberine* is produced; the *acid* l-*tartrate*, m. p. 219—224° (decomp.), $[\alpha]_D^{20}$ +150° in water, crystallises in groups of needles. By applying methyl sulphate in excess to methylcorytuberine methosulphate and neutralising the solution from time to time as it becomes acid, complete methylation of the alkaloid was eventually secured, and from the *dimethylcorytuberine methosulphate* formed, a small amount of the corresponding *methochloride* was prepared; it crystallises as needles, m. p. 234—237° (decomp.), $[\alpha]_D^{20}$ +197·4° in water, and gives an *aurichloride*, m. p. 160° (decomp.). The crude methosulphate on treatment with alkali gives *dimethylcorytuberimethine*, $C_{22}H_{27}O_4N$, the *hydrochloride* of which is crystalline and optically inactive. The methine base forms a *methiodide*, which melts above 260°, and a *methosulphate* (yellow needles); the latter, on treatment with alkali, furnishes trimethylamine and 3 : 4 : 5 : 6 - *tetramethoxy* - 8 - *vinylphenanthrene*, m. p. 69°, which on bromination in chloroform yields a *pentabromo*-derivative, $C_{20}H_{17}O_4Br_5$, m. p. 175—178°, and a *hexabromo*-compound, $C_{20}H_{16}O_4Br_6$, m. p. 185° (decomp.); the latter, on recrystallisation from acetic acid, gives a *pentabromo*-derivative, $C_{20}H_{17}O_4Br_5$, m. p. 185° (decomp.). On distillation with zinc dust, tetramethoxyvinylphenanthrene yields α-ethylphenanthrene (Pschorr and Karo, *loc. cit.*), and on oxidation with permanganate in acetone gives 3 : 4 : 5 : 6-*tetramethoxyphenanthrene*-8-*carboxylic acid*, m. p. 165—167°, crystallising in leaflets from alcohol, along with a small amount of a neutral substance, which is probably the corresponding glycol (compare Pschorr and Karo, *loc. cit.*). T. A. H.

Corydalis Alkaloids. XII. Corydine. *iso*Corydine. JOHANNES GADAMER (*Arch. Pharm.*, 1911, **249**, 669—680).—In part IX of this series of papers (Abstr., 1911, i, 1011), formulæ for corydine and *iso*corydine were given, based on the fact that they are monomethyl ethers of corytuberine, and are produced by the methylation of the latter alkaloid with diazomethane (see preceding abstract). In this paper the experimental details of this work are given. In a previous paper (Abstr., 1902, i, 391) the formula $C_{21}H_{23}O_4N$ or

$C_{21}H_{25}O_4N$

was assigned to corydine, but this is untenable in view of its relationship to corytuberine. New analyses of natural and synthetic corydine give results in agreement with the formula $C_{20}H_{23}O_4N$. When crystallised from alcohol, corydine contains ½EtOH, and then melts at 124—125°; on exposure in a vacuous desiccator and recrystallisation from ether, it melts at 149°. These two kinds of crystals are identical in form both for synthetic and natural corydine [$a : c = 1 : 0{\cdot}39896$]. On treatment with methyl iodide in the cold, corydine gives a *methiodide*, m. p. 190—191°, $[\alpha]_D^{20}$ +157·3° in 50% alcohol, crystallising in slender, voluminous needles with $1\frac{1}{2}H_2O$. If the mixture is heated, the methiodide formed has m. p. over 200°, $[\alpha]_D^{20}$ +154·6°, and forms compact crystals with $1\frac{1}{2}H_2O$.

On treatment with iodine in alcohol, corydine furnishes *dehydrocorydine hydriodide*, $C_{20}H_{19}O_4N,HI$, which separates from water in yellow, compact crystals and gives a red coloration, and eventually a flocculent, red precipitate, with solutions of sodium hydroxide. On reduction with zinc and dilute sulphuric acid, it gives dl-*corydine*, m. p. 165—167°, which is somewhat less soluble in ether than the optically-active forms. The acid *d*-tartrate, on crystallisation from water, deposits l-*corydine hydrogen* d-*tartrate*, from which l-*corydine*, $[\alpha]_D^{20}$ −206·2° in chloroform, was prepared.

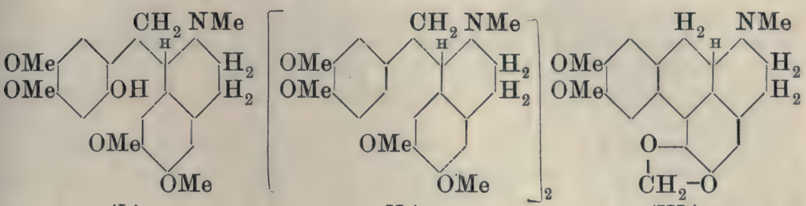
iso*Corydine*, $C_{20}H_{23}O_4N$, m. p. 185°, $[\alpha]_D^{20}$ +195·3° in chloroform, prepared as described already (see preceding abstract), crystallises in glistening, four-sided tablets, and is less soluble in ether than corydine. In its colour reactions it resembles bulbocapnine rather than corydine. The *methiodide*, m. p. 213—214° (decomp.), $[\alpha]_D^{20}$ +143·3°, is crystalline, and, unlike the corresponding corydine derivative, is sparingly soluble in water. On treatment with iodine in alcohol, *iso*corydine gives a greenish-black product.

T. A. H.

Corydalis Alkaloids. XIII. Glaucine Sub-group. JOHANNES GADAMER (*Arch. Pharm.*, 1911, **249**, 680—701).—Pschorr has described (Abstr., 1904, i, 612) the synthesis of phenanthreno-*N*-methyltetrahydropapaverine from *dl*-aminolaudanosine (amino-*N*-methyltetrahydropapaverine), but the substance he described under this name was probably *dl*-laudanosine, since it gave a methiodide, m. p. 215°. The author has repeated Pschorr's work, and finds that phenanthreno-*N*-methyltetrahydropapaverine is actually produced in this synthesis, and is *dl*-glaucine; in addition, the *dl*-forms of laudanosine, hydroxylaudanosine, and dilaudanosine are also formed. Formulæ for aminolaudanosine, laudanosine, and glaucine have been printed already (Abstr., 1900, i, 685; 1904, i, 612), and constitutions are now assigned to hydroxylaudanosine (I), dilaudanosine (II), and dicentrine (III), to which allusion is made later.

The solution resulting from the addition of copper powder to a diazotised solution of aminolaudanosine (Pschorr, *loc. cit.*) is reduced with zinc and dilute sulphuric acid; excess of ammonia is then added, and the solution shaken with ether, which removes all the alkaloids. The residue left on distilling the ether is separated into phenolic base (hydroxylaudanosine) and non-phenolic bases (laudanosine,

glaucine, and dilaudanosine) by solution in dilute hydrochloric acid and treatment of this liquid with excess of alkali hydroxide. Full



(I.) II.) (III.)

details of the isolation of these constituents from these two fractions are given.

dl-*Glaucine*, $C_{21}H_{25}O_4N$, m. p. 137—139°, gives a crystalline hydrochloride, which is less soluble than those of the *d*- and *l*-forms; the *methiodide*, m. p. 218—220°, is crystalline. dl-*Glaucine hydrogen* d- or l-*tartrate* crystallises in needles, and has $[\alpha]_D$ ± 33°. On recrystallisation from water these tartrates yield the corresponding salts of *d*- and *l*-glaucine, from which the free bases are obtainable; the *d*-glaucine so obtained is identical with the natural alkaloid (Fischer, Abstr., 1901, i, 743).

dl-Laudanosine, obtained in this reaction, is identical with that described by Pictet and Athanasescu (Abstr., 1900, i, 685).

dl-*Hydroxylaudanosine*, $C_{21}H_{27}O_5N$, m. p. 189—190·5° (decomp.), gives colour reactions resembling those of glaucine. By recrystallisation of the hydrogen tartrates it was separated into *d*- and *l*-forms. These crystallise in masses of long, colourless needles, and have m. p. 188—190·5° and $[\alpha]_D$ ± 50°. The *nitrates* crystallise well, and are sparingly soluble.

dl-*Dilaudanosine*, $C_{42}H_{52}O_8N_2$, is amorphous; it is produced in very small quantity in this synthesis, and was not obtained pure. Its chief colour reactions are described.

Dicentrine, isolated by Asahina (Abstr., 1909, i, 601), closely resembles glaucine in its colour reactions, physiological action, and chemical properties, and for that reason is regarded as glaucine, in which the ‒OMe groups in positions 5 and 6 are replaced by a dioxymethylene group. A synthesis of dicentrine is being attempted.

T. A. H.

Isomerism of Corynanthine with Yohimbine. Ernest Fourneau and Fiore (*Bull. Soc. chim.*, 1911, [iv], 9, 1037—1040).—In view of the possible isomerism of these two alkaloids already referred to (Abstr., 1910, i, 501), the authors have re-examined yohimbine, and find that, like corynanthine, it has the composition represented by the formula $C_{21}H_{26}O_3N_2$. Yohimbine hydrochloride has $[\alpha]_D^{20}$ +105°; corynanthine hydrochloride has $[\alpha]_D^{20}$ −64·15°. T. A. H.

Red Compounds from Brucine. Josef Buraczewski and Z. Zbijewski (*Bull. Acad. Sci. Cracow*, 1911, *A*, 464—469).—Various reagents act on brucine to give red soluble compounds without oxidising or decomposing the brucine molecule.

By the action of dry chlorine on brucine, until the evolution of hydrogen chloride begins, a reddish-brown substance,

$$C_{22}H_{22}O_4N_2Cl_2,HCl,2H_2O,$$

is obtained. When the action of the chlorine is prolonged until no more hydrogen chloride separates, a dark grey *powder* is obtained, soluble in water with a red coloration; this has the composition $C_{21}H_{19}O_4N_2Cl_3,HCl,2H_2O$.

When bromine is allowed to act on brucine in absolute alcohol, a brownish-red *powder* is obtained, which is considered to be a mixture of $C_{21}H_{22}O_4N_2Br,2H_2O$ and $C_{22}H_{24}O_4N_2Br,HBr,H_2O$.

The production of a red coloration when the product of the action of dry chlorine on brucine is boiled with alcohol is characteristic of this alkaloid, and may be used for its detection. E. F. A.

Hæmopyrrole. HANS FISCHER and E. BARTHOLOMÄUS (*Ber.*, 1911, **44**, 3313—3317).—Knorr and Hess have recently published (Abstr., 1911, i, 1019) a synthesis of 2 : 4-dimethyl-3-ethylpyrrole which they consider not to be identical with hæmopyrrole investigated by Piloty (Abstr., 1910, i, 133). The main difference is a discrepancy of 23° in the melting point of the picrates.

The authors show that hæmopyrrole picrate has m. p. 120—122°, instead of 108·5° as previously described. In attempting to obtain 2 : 4-dimethyl-3-ethylpyrrole according to the method of Knorr and Hess, the authors obtained, in place of the expected hydrazone, a ketazine, the m. p. of which varied between 195° and 215°. This, on energetic reduction, yields an oil, the b. p. of which agreed with that given by Knorr and Hess, but the picrate melted indefinitely at 82—83°. This oil, when treated with benzenediazonium sulphate, yielded an *azo-dye*, $C_{14}H_{17}O_3N_3S$, which crystallises in red needles (compare this vol., i, 41, 56). H. W.

Picrylpyridinium Chloride. MAX BUSCH and WALTER KÖGEL (*J. pr. Chem.*, 1911, [ii], **84**, 507—514).—When equal molecular quantities are heated in alcohol on the water-bath, picryl chloride and pyridine yield at first a little *picrylpyridinium picrate*, yellow needles, m. p. 223°, and finally, after cooling, almost colourless crystals of *picrylpyridinium chloride*, $C_5H_5N{<}^{Cl}_{C_6H_2(NO_2)_3}$, m. p. 128°; the latter changes to the former after long keeping, or after prolonged boiling in alcoholic solution. The chloride is converted by alcoholic potassium hydroxide into the *potassium* salt of a pyridine dye, probably $NO_2K{:}C_6H_2(NO_2)_2{:}NC_4H_4{\cdot}CHO$, which forms reddish-brown crystals with a green lustre. Picrylpyridinium picrate is decomposed almost quantitatively into pyridine and picric acid by boiling water, and yields with potassium iodide, *picrylpyridinium iodide*, m. p. 155°, orange leaflets. In ether, pyridine and picryl chloride (2 mols.) yield an additive *compound*, $C_{11}H_7O_6N_4Cl,C_6H_2(NO_2)_3Cl$, m. p. 151°, yellowish-green needles. C. S.

New Derivatives of Dioxindole. MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1911, **32**, 905—916).—Various substituted dioxindoles with a tertiary hydroxyl group have already been obtained

by the application of the Grignard reagent to isatin (Kohn, Abstr., 1910, i, 697).

3-Phenyldioxindole by methylation with methyl sulphate gives *3-phenyl-1-methyldioxindole methyl ether*; this forms leafy crystals, m. p. 83°. The action of acetic anhydride yields a monoacetyl compound, probably *1-acetyl-3-phenyldioxindole*, which crystallises from benzene in short, columnar crystals, m. p. 141°.

3-Benzyl-1-methyldioxindole methyl ether, obtained analogously to the corresponding phenyl compound, forms needles, m. p. 97°.

3-Methyldioxindole, obtained by the action of magnesium methyl iodide on isatin, forms white, granular crystals, m. p. 160°; methylation gives 1 : *3-dimethyldioxindole methyl ether*, cubical crystals, m. p. 78·5°; it yields a *diacetyl* derivative, m. p. 125°.

5-Bromo-3-phenyldioxindole is produced when magnesium phenyl bromide reacts with 5-bromoisatin; it forms thin rods, m. p. 243° with decomposition.

5-Bromo-3-methyldioxindole is obtained similarly from bromoisatin with magnesium methyl iodide, and also by the action of bromine water on 3-methyldioxindole; on heating it turns brown at 240°, and melts at 258°. When methylated, it produces *5-bromo-1 : 3-dimethyldioxindole methyl ether*, needles, m. p. 142°. D. F. T.

Spirans. IV. History and Theory. Dan Radulescu (*Chem. Zentr.*, 1911, 82, ii, 1535; from *Bull. Soc. Sti. Bucuresti*, 1911, 20, 281—284. Compare Abstr., 1911, i, 497).—The chemical properties of a spiran ACB, composed of rings CA and CB of known structure and properties, are qualitatively the sum of those due to AC and CB, except where there are large accumulations of groups on the same carbon atom. With the exception of those formed from three or four atom rings, the spirans are stable. They show optical activity in some cases, although no asymmetric atom is present. Compounds in which two rings share a common nitrogen atom are quite different from the spirans, although they present a superficial resemblance to them.

T. A. H.

Compounds of Ferric Salts with Antipyrine. Filippo Calzolari (*Boll. chim. farm.*, 1911, 50, 763—767).—The molecular weight of antipyrine, determined cryoscopically in aqueous solutions, is normal, but when ferric chloride is present higher values are obtained, so that the red coloration which antipyrine gives with ferric chloride is probably due to the formation of a complex cation. Ferric fluoride gives only a pale yellow coloration with antipyrine, and corresponding with this the molecular weight of antipyrine is lower in this solution than in the presence of ferric chloride. The *compound* of ferric chloride and antipyrine is an orange-red, crystalline powder having the composition $2FeCl_3,3C_{11}H_{12}ON_2$, and ferric bromide also yields a *compound*, $2FeBr_3,3C_{11}H_{12}ON_2$, which forms reddish-brown crystals. R. V. S.

1-Phenyl-3-methyl-5-pyrazolone and 4-Amino-1-phenyl-3-methyl-5-pyrazolone. Alfred Heiduschka and O. Rothacker (*J. pr. Chem.*, 1911, [ii], 84, 533—542).—The heating of 1-phenyl-

3-methyl-5-pyrazolone and *o*-, *m*-, or *p*-nitrobenzaldehyde at 140° for ten minutes yields a mixture of the nitrobenzylidene derivative and a bispyrazolone derivative, which is separated by means of benzene. 4-o-*Nitrobenzylidene*-1-*phenyl*-3-*methyl*-5-*pyrazolone*, m. p. 157°, crystallises in red needles; the corresponding meta- and para-isomerides have m. p. 162° and 171° respectively. 4 : 4′-o-*Nitrobenzylidenebis*-1-*phenyl*-3-*methyl*-5-*pyrazolone*, $NO_2\cdot C_6H_4\cdot CH(C_{10}H_9ON_2)_2$, m. p. 146° (decomp.), and the meta-isomeride, m. p. 150° (decomp.), form yellow leaflets.

When heated with zinc chloride at 140°, 1-phenyl-3-methyl-5-pyrazolone condenses with acetophenone to form 1-*phenyl*-4-*a*-*phenylethylidene*-3-*methyl*-5-*pyrazolone*, $CMePh\colon C<\begin{matrix}CO-NPh\\ CMe\colon N\end{matrix}$, m. p. 89°, orange crystals, and with benzophenone to form a corresponding *substance*, $C_{23}H_{18}ON_2$, m. p. 133°, orange-red leaflets.

4-Amino-1-phenyl-3-methyl-5-pyrazolone reacts with cinnamaldehyde and with *o*-nitrobenzaldehyde to form the corresponding Schiff's *bases*, $C_{19}H_{17}ON_3$, m. p. 192°, and $C_{17}H_{14}O_3N_4$, m. p. 198°. Also with piperonal and with anisaldehyde it yields the *substances*, $C_{44}H_{36}O_9N_6$, m. p. 235°, and $C_{44}H_{42}O_6N_6$, m. p. 252°, respectively. C. S.

Conversion of the Nitro- into the Keto-group. WILHELM WISLICENUS and HERMANN GÖZ (*Ber*., 1911, **44**, 3491—3496).—The *potassium* salt of 4-oximino-1-phenyl-3-methyl-5-pyrazolone separates in lustrous, silky, deep yellow needles, m. p. 250—255°. By the action of bromine, 4-*bromo*-4-*nitro*-1-p-*bromophenyl*-3-*methyl*-5-*pyrazolone* is formed; this crystallises in well formed, small, dark yellow prisms, m. p. about 85°, to a red oil (decomp.). On heating, it is converted into 4-*keto*-1-p-*bromophenyl*-3-*methyl*-5-*pyrazolone*,

$$C_6H_4Br\cdot N<\begin{matrix}CO\cdot CO\\ N-CMe\end{matrix};$$

this separates in small, flat prisms, yellowish-red in transparent, bluish-red in reflected, light, m. p. after sintering 171—172°. On boiling with water, it forms colourless needles, probably indicating an additive product; a colourless additive product is formed also with sodium hydrogen sulphite.

When dissolved in sodium hydroxide or carbonate the keto-pyrazolone ring is opened; from the reddish-yellow solution a yellow acid is precipitated by strong mineral acids. This *aβ-diketobutyric acid β*-p-*bromophenylhydrazone*, $C_6H_4Br\cdot NH\cdot N\colon CMe\cdot CO\cdot CO_2H$, crystallises in microscopic, canary-yellow prisms, m. p. 153—154° (decomp.). On boiling with acetic anhydride the deep red keto-*p*-bromophenylmethylpyrazolone is re-formed. With phenylhydrazine a golden-yellow *phenylosazone*, m. p. 211°, is obtained. The yellow insoluble *silver* salt reacts with methyl iodide to form the methyl ester,

$$C_6H_4Br\cdot NH\cdot N\colon CMe\cdot CO\cdot CO_2Me,$$

which crystallises in brownish-yellow, microscopic prisms, m. p. 165—170°.

When warmed for several days with acetic acid, keto-*p*-bromophenylmethylpyrazolone is converted into *dibromorubazonic acid*,

$$C_6H_4Br\cdot N<\begin{matrix}N=CMe\\ CO\cdot CH\cdot N=\end{matrix}\begin{matrix}CMe\colon N\\ C-CO\end{matrix}>N\cdot C_6H_4Br.$$

This has m. p. 305—308°, and dissolves in alcoholic potassium hydroxide and in concentrated ammonia with a violet-red coloration.

4-*Bromo-4-nitro-3-methyl-5-pyrazolone*, $NH<\begin{matrix}N{=}CMe\\ CO\cdot CBr\cdot NO_2\end{matrix}$, obtained from the golden-yellow prisms of the potassium salt of 3-methyl-4-*iso*nitro-5-pyrazolone, crystallises in small, yellowish-white prisms, m. p. 84—85° (decomp.). On heating, a red, amorphous substance is obtained, which could not be purified. E. F. A.

Hydantoins. VII. Synthesis of 2-Thiohydantoin. TREAT B. JOHNSON and BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1911, **33**, 1973—1978).—2-Thiohydantoin has been synthesised by Komatsu (Abstr., 1911, i, 683) by the action of potassium thiocyanate on glycine in presence of acetic anhydride, and also by Wheeler, Nicolet, and Johnson (Abstr., 1911, i, 1031) by heating acylthiohydantoic acids with hydrochloric acid.

A large quantity of 2-thiohydantoin being required for certain investigations, Komatsu's method was employed, and it was found that the compound could be very easily prepared in this way. Komatsu's interpretation of the mechanism of the reaction is incorrect, and his statement that thiohydantoic acid is produced could not be confirmed. It is shown that acetylglycine is first produced, and combines with thiocyanic acid to form a thiocyanate, which undergoes re-arrangement to acetylthiohydantoic acid. This compound suffers an inner condensation, with formation of 2-thio-3-acetylhydantoin, which is subsequently converted into 2-thiohydantoin.

When glycine is heated with potassium thiocyanate and acetic anhydride, 2-*thio-3-acetylhydantoin*, $CH_2<\begin{matrix}CO{-}NH\\ NAc\cdot CS\end{matrix}$, m. p. 175—176°, is produced, which crystallises in square blocks, and when heated with hydrochloric acid is converted quantitatively into 2-thiohydantoin. The compound can also be obtained by the action of potassium thiocyanate on acetylglycine (aceturic acid).

By the action of potassium thiocyanate on hippuric acid in presence of acetic anhydride (9 parts) and glacial acetic acid (1 part), 2-*thio-3-benzoylhydantoin*, $CH_2<\begin{matrix}CO{-}NH\\ NBz\cdot CS\end{matrix}$, m. p. 165°, is obtained in a yield of 86%; it crystallises in square plates. When the compound is hydrolysed with concentrated hydrochloric acid, it yields 2-thiohydantoin, and when condensed with benzaldehyde in presence of glacial acetic acid and anhydrous sodium acetate, it is converted into 2-thio-4-benzylidenehydantoin. E. G.

Condensation of Methyluracil and Formaldehyde. WILHELM KIRCHER (*Annalen*, 1911, **385**, 293—314).—4-Methyluracil and 40% formaldehyde (3 mols.) condense in acid solution to form 4-*methyl-5-hydroxymethyluracil*, $CO<\begin{matrix}NH{-}CO\\ NH\cdot CMe\end{matrix}>C\cdot CH_2\cdot OH$, plates or needles, decomp. 305—310°; in alkaline solution, the same product is obtained in the form of the *sodium* salt, $C_6H_7O_3N_2Na$. The substance is

reconverted into its generators by boiling water, and is changed to a substance, $C_{12}H_{14}O_5N_4$, decomp. 303—307°, by boiling dilute hydrochloric acid. By reduction with tin and 36% hydrochloric acid at 58—60°, it yields 4 : 5-dimethyluracil and a substance, $C_{11}H_{12}O_4N_4$ decomp. 302—307°. 4 : 5-Dimethyluracil has also been prepared by passing the vapour of cyanic acid (3 mols.) in a current of dry carbon dioxide into an ethereal solution of methyl β-amino-α-methylcrotonate in a freezing mixture, boiling the product with 10% potassium hydroxide, and acidifying after the removal of the cyamelide by filtration. 4 : 5-Dimethyluracil is oxidised to acetylcarbamide and oxalic acid by 4% potassium permanganate, and when heated with aqueous potassium hydroxide, 95% alcohol, and methyl iodide yields a mixture of 1 : 3 : 4 : 5-*tetramethyluracil*, m. p. 123—125·5°, 1 : 4 : 5-*trimethyluracil*, m. p. 220·5—222°, and 3 : 4 : 5-*trimethyluracil*, m. p. 172—174°.

A suspension of 4 : 5-dimethyluracil is converted by bromine into 4-*bromo*-5-*hydroxy*-4 : 5-*dimethyldihydrouracil*,

$$CO<\begin{matrix}NH\text{———}CO\\NH\cdot CMeBr\end{matrix}>CMe\cdot OH,$$

m. p. 226—227° (decomp.), which changes to 4-*bromo*-4-*methyl*-5-*methylenedihydrouracil* at 105°, and to 4-*bromo*-5-*ethoxy*-4 : 5-*dimethyldihydrouracil*, m. p. 225—226° (decomp.), when boiled with alcohol. The last substance at 105° also yields 4-bromo-4-methyl-5-methylenedihydrouracil, which is converted by bromine water into 4-*bromo*-5-*hydroxy*-4-*methyl*-5-*bromomethyldihydrouracil*, $C_6H_8O_3N_2Br_2$, m. p. 165—167° (decomp.); the latter is also obtained by treating 4 : 5-dimethyluracil with bromine and subsequently boiling with water.

When 4-bromo-5-hydroxy-4 : 5-dimethyldihydrouracil is treated with 5% potassium hydroxide in the cold, a substance, $C_6H_{10}O_4N_2,H_2O$, m. p. 168·5—169·5° (decomp.), is obtained, which may be 4 : 5-dihydroxy-4 : 5-dimethyldihydrouracil or acetylmethylhydantoin (compare Bremer, Abstr., 1911, i, 160). C. S.

Alkyl Derivatives of Methyluracil. OSKAR BÜCKENDORFF (*Annalen*, 1911, **385**, 314—327).—4-Methyl-3-ethyluracil (Hoebel, Abstr., 1907, i, 557) reacts with aqueous bromine to form 5 : 5-*dibromo*-4-*hydroxy*-4-*methyl*-3-*ethyldihydrouracil*, $NEt<\begin{matrix}CO\text{————}NH\\CMe(OH)\cdot CBr_2\end{matrix}>CO$, m. p. about 160°, which is converted by 95% alcohol into 5-*bromo*-4-*methyl*-3-*ethyluracil*, m. p. 234—236° (decomp.); the latter reacts with aqueous ammonia at 150—160° to form 5-*amino*-4-*methyl*-3-*ethyluracil*, m. p. 234—236°. The following compounds are obtained from 4-methyl-1-ethyluracil by similar methods: 5 : 5-*dibromo*-4-*hydroxy*-4-*methyl*-1-*ethyldihydrouracil*, m. p. about 160°; 5-*bromo*-4-*methyl*-1-*ethyluracil*, m. p. 203—206°; 5-*amino*-4-*methyl*-1-*ethyluracil*, m. p. 203—205°. 4-Methyl-1-ethyluracil is converted by sulphuric and nitric acids on the water-bath into 5-*nitro*-1-*ethyluracil*-4-*carboxylic acid*, $C_7H_7O_6N_3,H_2O$, m. p. 189° (decomp.), and a *substance*, $C_7H_6O_5N_4$, decomp. 180—220°; at 140—150° the former yields 5-*nitro*-1-*ethyluracil*, m. p. 159—161°, which is reduced by aqueous ammonia and aluminium amalgam to 5-*amino*-1-*ethyluracil*, m. p. 171—172°.

4-*Methyl*-3-*propyluracil*, m. p. 170—172°, and 4-*methyl*-1-*propyluracil*, m. p. 184°, are prepared and separated in a similar manner to the methylethyluracils (Hoebel, *loc. cit.*). Their constitutions are proved as follows: 4-Methyl-1-propyluracil by ethylation, and 4-methyl-3-ethyluracil by propylation, yield the same 4-*methyl*-3-*ethyl*-1-*propyluracil*, m. p. 63—65°. Also, 4-methyl-1-propyluracil by methylation, and 3 : 4-dimethyluracil by propylation, yield the same 3 : 4-*dimethyl*-1-*propyluracil*, m. p. 85—87°. Finally, 4-methyl-3-propyluracil by methylation, and 1 : 4-dimethyluracil by propylation, yield the same 1 : 4-*dimethyl*-3-*propyluracil*, m. p. 52—54°.

Methylallyluracils have been prepared and their constitutions proved by similar methods. 4-*Methyl*-1-*allyluracil* and 4-*methyl*-3-*allyluracil* have m. p. 180—182° and 168—169° respectively; 1 : 4-*dimethyl*-3-*allyluracil* and 3 : 4-*dimethyl*-1-*allyluracil* have m. p. 45—47° and 59—61° respectively.

*Methyl*iso*butyluracils*, m. p. 195—196° and 133—135°, have been obtained, but have not yet been fully investigated. C. S.

Phenylmethyltriazole. A Correction. EUGEN BAMBERGER (*Ber.*, 1911, **44**, 3564—3565).—It was previously stated (Abstr., 1894, i, 23) that 1-phenyl-5-methyltriazole-3-carboxylic acid yielded phenylmethyltriazole, m. p. 191°, when heated in a stream of carbon dioxide. Pellizzari has shown that this compound is in reality cyanophenylacetamidine, NPh:CMe·NH·CN. It was also stated that the compound was a base, but it is now shown to be an acid soluble in sodium hydroxide, and is precipitated in colourless needles, as stated by Pellizzari (*loc. cit.*). E. F. A.

***N*-Quinhydrones.** M. M. RICHTER (*Ber.*, 1911, **44**, 3466—3469).—The action of iodine on *p*-phenylenediamine in benzene solution gives rise to an almost black substance of the composition

$$NH:C_6H_4:NH,NH_2\cdot C_6H_4\cdot NH_2,2HI,I_2,$$

a nitrogen analogue of the quinhydrones. This N-*benzoquinhydrone dihydriodide periodide* is an almost black substance, which loses iodine on warming. On account of its instability, the corresponding base could not be isolated.

Benzidine treated with iodine in a similar manner gives N-*benzidinequinhydrone dihydriodide periodide*, $C_{24}H_{22}N_4,2HI,I_4$, a greyish-black powder, which loses iodine even at the ordinary temperature.

o-Phenylenediamine treated with iodine behaves quite differently, and yields 2 : 3-diaminophenazine.

References are given to papers describing compounds which must be regarded as derived from the above bases or from bases of the same type. The author ascribes to all these bases a structure analogous to that which he has already attributed to the quinhydrones (Abstr., 1911, i, 136), for example, $NH:C_6H_4:NH_2\cdot NH\cdot C_6H_4\cdot NH_2,2HI.I_2$.

D. F. T.

Preparation of Solid Diazonium Salts by means of Nitrosyl Chloride. M. STRUSZYŃSKI and WOJEIECH SVENTOSLAVSKY (*Bull. Acad. Sci. Cracow*, 1911, *A*, 459—463).—Nitrosyl chloride, which is now an

easily accessible product, is an energetic diazotising agent, and it is conveniently used for preparing solid diazonium salts in a state of purity.

The amine is dissolved in alcohol, and an alcoholic solution of hydrogen chloride containing 2·5—3 mols. of the acid added; the mixture is cooled in ice, and the solution of nitrosyl chloride in toluene added. Action is rapid and complete, and the insoluble diazonium salt separates. When sulphuric acid is substituted for hydrochloric acid, the corresponding sulphates are obtained. E. F. A.

Cazeneuve's Diphenylcarbodiazide and Diphenylcarbazone. EUGEN BAMBERGER (*Ber.*, 1911, **44**, 3743—3754).—From a comparison of the properties, the author shows that the diphenylcarbodiazide of Cazeneuve (Abstr., 1901, i, 297) is identical with the betaine of diphenylhydroxytetrazolium hydroxide (Bamberger, Abstr., 1899, i, 355); the latter name gives the correct description.

Reasons are also given for believing that whilst the formula $N_2Ph\cdot CO\cdot NH\cdot NHPh$ correctly represents the structure of free diphenylcarbazone (compare Heller, Abstr., 1891, 1212), the salts, which have a much more intense colour, are derived from the structure $N_2Ph\cdot C(OH){:}N\cdot NHPh$. D. F. T.

Hæmopyrrole. LAD. LEYKO and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1911, *A*, 345—349).—The hydrochlorides of dyes obtained by coupling hæmopyrrole with benzenediazonium chloride have been described previously (Leyko and Marchlewski, Abstr., 1910, i, 144). To obtain the free base, $N_2Ph\cdot C_8H_9N\cdot N_2Ph$, the hydrochloride is decomposed with sodium acetate in alcoholic solution.

Bisbenzeneazohaemopyrrole forms fine, lustrous needles, m. p. 171—172°. In ethereal solution it shows two absorption bands in the visible region of the spectrum, whereas biscymeneazopyrrole and bisbenzeneazopyrrole are characterised by only one band. Taking into account Küster's proof that hæmopyrrole, $C_8H_{13}N$, yields methylethylmaleinimide on oxidation, the bisbenzeneazo-derivative is formulated as $PhN_2\cdot N{<}\begin{matrix}CMe{=\!=}CEt\\ \quad\;\;|\\ C(N_2Ph){:}CMe\end{matrix}$ [compare this vol., i, 41, 50]. E. F. A.

The Changes in Physical Conditions of Colloids. XII. The Properties of the Protein Ions. CARL SCHORR (*Biochem Zeitsch.*, 1911, **37**, 424—451).—According to the theory of Pauli, proteins act both as acids and bases, but under certain conditions of hydrogen ion concentration, the protein ions themselves exist in solution, and not protein salts of either acids or bases. The protein ions, according to the theory, differ from the protein salts in that the ions, as hydrophil colloids, are capable of existing as highly hydrated aggregates, from which the water is extracted only with some difficulty. This theory is supported by the fact that under such conditions the solution of protein contains protein not in form of salts; the protein is only slightly, if at all, precipitated by dehydrating agents, such as alcohol. Such solutions, furthermore, owing to the large aggregates, have a high viscosity, and also, owing to the large size of the hydrated

protein ions and their slow motion, have only a relatively small capacity for conducting electricity. In the presence of neutral salts, furthermore, the protein ions lose their electric charge, and all those properties disappear which are due to the presence of protein ions. In the presence of salts there is therefore a restitution of such properties as the precipitability by alcohol and a diminution of viscosity. The above theory is substantiated by numerous experiments on the precipitability of proteins in the presence of varying quantities of acids and bases, and by numerous physical measurements of the properties of the solutions under the varying conditions.

S. B. S.

Action of Bromine and Iodine on Proteins. A. Krzemecki (*Bull. Acad. Sci. Cracow*, 1911, *A*, 470—488).—Previous observers of the action of iodine or bromine on proteins have worked under conditions in which more or less oxidation took place. The experiments now described were made so as to alter the protein molecule as little as possible, merely introducing halogen partly in a very loosely bound condition.

Egg-albumin was found to retain 28·3—29·6% of iodine and 18% of bromine, serum-albumin 28·5% iodine and 20·5% bromine, casein 19·1 to 24·9% iodine, and plant protein 34·6% iodine. The halogen is attached to the protein molecule in several different ways, part being removed by boiling with acetic acid; thus, after treatment, egg-albumin contains 24·45% iodine, serum-albumin 24·5% iodine, and casein 17·37% iodine. Acetone at the ordinary temperature eliminates a further proportion of halogen, egg-albumin now containing 15·6% iodine, and serum-albumin 14%. Finally, treatment with sodium thiosulphate reduced the iodine in egg-albumin to 6·26%.

α-Hydroxyprotosulphonic acid, under similar conditions, was only able to take up 11·12% of iodine when made from egg-albumin, and 9·8% of iodine when prepared from serum-albumin. When the halogen proteins are heated with water, a large amount of decomposition takes place. The halogen proteins are digested both by trypsin and pepsin.

The halogens in ethereal solution were allowed to act on the protein, absorption being usually complete within a few hours in the case of iodine. Even better results were obtained, using methyl alcohol as solvent.

E. F. A.

3 : 5-Di-iodotyrosine from Iodoprotein. IV. Gorgonin and Spongin. Adolf Oswald (*Zeitsch. physiol. Chem.*, 1911, **75**, 353—362).—The iodoproteins differ in the relative proportions of fixed iodine and iodine eliminated as hydrogen iodide on decomposition with barium hydroxide (compare Oswald, Abstr., 1911, 697, 842). Of the total iodine in gorgonin, 82% is fixed, and 18% can be eliminated; the amount of di-iodotyrosine isolated was 0·9%. Tyrosine is not the only iodine-fixing group of gorgonin. Spongin yields 64% of fixed iodine, 36% being eliminated on continued boiling; 15·7% of the total iodine was isolated in the form of di-iodotyrosine. Spongin is regarded as containing at least two forms of iodine compound.

E. F. A.

The Physical Chemistry of the Bence-Jones Protein. WOLFGANG PAULI (*Chem. Zentr.*, 1911, ii, 371; from *Zentr. Physiol.*, 1911, 25, 110—111).—The author, in view of the recent work of Hopkins and Savory on the Bence-Jones protein, calls attention to the fact that he has already explained the peculiar properties of this substance as regards its solubility in salt solutions as a special case of the general properties of proteins. S. B. S.

Formation and Estimation of Methæmoglobin. JOSEPH BARCROFT and FRANZ MÜLLER (*Proc. physiol. Soc.*, 1911, xx.; *J. Physiol.*, 43).—Methæmoglobin is formed quantitatively when potassium nitrite is added to blood, the amount of hæmoglobin converted containing an amount of dissociable oxygen equivalent to that necessary to convert nitrite into nitrate. Hydroxylamine sulphate acts similarly. Magnesium chlorate does not do so. Methæmoglobin in blood may be estimated by combining two operations: (1) a comparison of the oxygen capacity with that of a standard blood, and (2) colorimetric comparison of the blood for estimation with the same standard, the hæmoglobin in both being first turned into methæmoglobin. Two mild cases of methæmoglobin poisoning in cats produced no change in the dissociation curve of the blood. W. D. H.

Preparation of Nucleic Acid. AMOS W. PETERS (*J. Biol. Chem.*, 1911, 10, 373—379).—Barium hydroxide with sodium chloride is used for the extraction of the tissue. The alkalinity thus obtained is sufficient to decompose the nucleo-proteins. One advantage of this new method is the comparative insolubility of the barium compounds formed with constituents of the tissue, and so little protein goes into solution that a separate precipitation of protein is unnecessary. The solution of barium hydroxide and sodium chloride dissolves nucleic acid freely. Barium, proteins, and guanylic acid are absent from the final product. W. D. H.

Tyrosine as an Agent for the Fixation of Iodine in the Preparation of Iodopeptones. PAUL MACQUAIRE (*Compt. rend.*, 1911, 153, 1084—1085).—Di-iodotyrosine has been isolated from peptones which have been treated with iodine. W. O. W.

Oxyprotosulphonic Acids. I. JOSEF BURACZEWSKI and L. KRAUZE (*Zeitsch. physiol. Chem.*, 1911, 76, 37—43. Compare Abstr., 1911, i, 408).—Crude oxyprotosulphonic acid from egg-albumin, blood-serum, and casein is divided into fractions: (α) insoluble in hot acetic acid; (β) crystallising from acetic acid solution in the cold; (γ) soluble in acetic acid, insoluble in alcohol; (γ_2) insoluble in cold alcohol; (γ_3) soluble in alcohol, but precipitated by ether. Each of these fractions has been analysed completely; they differ in the intensity with which they show the biuret coloration, and also as regards the blackening with a lead salt due to sulphur in a loosely combined state. The intensity with each test falls from the α- to the γ_3-acid, that is, with the increase in solubility, and possibly corresponds with the increased

oxidation of the protein. The α-oxyprotosulphonic acid comprises more than one-half of the total product. E. F. A.

Hydrolytic Decomposition of Proteins by Pepsin, Trypsin, Acids, and Alkalis. VALDEMAR HENRIQUES and J. K. GJALDBÆK (*Zeitsch. physiol. Chem.*, 1911, 75, 363—409).—The hydrolysis of a number of proteins by pepsin and trypsin has been followed by Sörensen's method of titrating in presence of formaldehyde, the titration of the amino-acids being effected in four stages (Henriques and Sörensen, Abstr., 1910, ii, 164, 466). The liquid is made neutral to litmus paper, phenolphthalein added, and then *N*/5-sodium hydroxide until a faint red coloration is obtained (stage 1); the addition is continued until the deep red colour of the control is matched (stage 2), when the neutral formaldehyde solution is added, and the titration continued until a faint red (stage 3) and a deep red (stage 4) colour are obtained. The ratio of the figure in stage 4, less the alkali used in the control, to the figure in stage 1 is calculated for each test. The other determinations made were the total nitrogen, the nitrogen as ammonia, and the nitrogen which could be titrated as formaldehyde expressed as a percentage of the total.

Pepsin contains about 25% of titratable nitrogen; trypsin some 28%. On auto-digestion these figures increase to 37% and 58% respectively.

Egg-white, casein, lean beef, edestin, gliadin, gelatin, and Witte peptone were incubated with pepsin or trypsin, and the above measurements made every few days. With pepsin, after about one hundred and seven days' action, from 30—38% of the total nitrogen can be titrated with formaldehyde. The action of the pepsin itself very soon falls off and stops altogether, subsequent digestion being due to the action of the acid; accordingly, fresh pepsin was occasionally added. It is evident that the products of very prolonged peptic action are in the main due to the action of the acid present.

Much evidence as to the nature of the hydrolysis is given by the ratio of the alkali required in the 4th and 1st stages of titration. In the case of glycine this is 48·9; for glycyl-glycine it is only 2·1. Alanine has a value of 64·7; arginine, lysine, cystine, and tryptophan have values below 10; the values for aspartic acid, 162, and glutamic acid, 194, are very high. The formation of amino-acids during hydrolysis will therefore be indicated by a large increase in the value of the ratio.

The experiments with pepsin show a low value, 2·1—2·7, for the ratio, which does not materially change during hydrolysis, indicating that the products of hydrolysis are polypeptides and not amino-acids. The amount of ammonia formed increases throughout hydrolysis; it differs considerably in magnitude in the six proteins investigated, but is far larger in the case of pepsin and hydrochloric acid than with trypsin.

The trypsin experiments show variations of from 25% in the case of gelatin to 60% in the case of egg-white in the amount of nitrogen which can be titrated in presence of formaldehyde. The titration

ratio is, as a rule, larger with trypsin, being markedly so in the case of egg white, and it tends to increase during the progress of hydrolysis, indicating the formation of amino-acids. The results show clearly the differences between the action of the two ferments.

The addition of pepsin to the products of a completed tryptic hydrolysis slightly increased the amount of nitrogen which could be titrated, and tended to lessen the titration ratio. The addition of trypsin to a completed peptic digestion caused the greatest total hydrolysis measured, and an increase in the titration ratio, which, however, did not become so large as in the case of the simple tryptic digestion owing to the presence of the peptide constituents.

For comparison, hydrolysis has also been effected by hydrochloric acid and by sodium hydroxide. The proportion of ammonia formed is greatest in the last case. The titration ratio indicates that acid hydrolysis is very similar to that caused by pepsin; possibly pepsin acts as a catalyst for the weak acid. The titration ratio is higher in hydrolysis by alkali, but not as great as with trypsin; probably the difference in the mode of action in the two agents depends mainly on the secondary changes produced by the alkali.

E. F. A.

Inactivation of Trypsin by Dialysis against Distilled Water; Reactivation of the Diastase by Addition of Salts. ALBERT FROUIN and ARTHUR COMPTON (*Compt. rend.*, 1911, **153**, 1032—1034). —The proteolytic enzyme of pancreatic juice is rendered inactive when the liquid is submitted to dialysis for sixty-six to seventy-two hours, but can be activated by addition of certain salts, such as sodium chloride, bromide, iodide, fluoride, acetate, citrate, magnesium sulphate, and others, or by alkali hydroxides. If dialysis is prolonged beyond the period stated, the enzyme undergoes a permanent loss of activity.

W. O. W.

Protection of Trypsin from Destruction by Heat. D. H. DE SOUZA (*J. Physiol.*, 1911, **43**, 374—378).—A temperature of 80° destroys trypsin in five minutes; the protective action of peptone in the solution is very slight, but rather greater if the reaction is acid or neutral. Lower temperatures (65—70°) take longer to destroy the enzyme, and the protective action of peptone is somewhat greater. The protection is too small to be of any value in sterilising enzymes by heat. Experiments without antiseptics are not trustworthy.

W. D. H.

Tryptic Digestion of Silk. I. W. S. HUBBARD (*J. Amer. Chem. Soc.*, 1911, **33**, 2032—2035).—Experiments are described which show that silk is slowly hydrolysed by trypsin with formation of tyrosine, tryptophan, or a compound of this substance, and dextrorotatory tryptic peptones.

E. G.

The Conditions for Optimal Action of Invertase. ARISTIDES KANITZ (*Biochem. Zeitsch.*, 1911, **37**, 50—51).—In view of various recent investigations on this subject, the author calls attention to his own work published in 1903, in which he showed that the optimal action

of invertin from *Aspergillus niger* takes place in a medium with hydrogen ion concentration of $3 \cdot 3 \times 10^{-3}$ to $3 \cdot 3 \times 10^{-4}$ at a temperature of 56° (compare Abstr., 1904, i, 158). S. B. S.

Mechanism of the Destruction of Diastases by Light. HENRI AGULHON (*Compt. rend.*, 1911, **153**, 979—982. Compare this vol., ii, 243).—Enzymes are divisible into three classes according to their sensitiveness to light. Sucrase, tyrosinase, and laccase are destroyed by visible rays only in presence of oxygen; in a vacuum they are destroyed only by ultra-violet light. Probably in the absence of molecular oxygen, hydrogen peroxide is the effective agent of decomposition. Emulsin and catalase are destroyed by light of all wave-lengths, even in a vacuum, but more rapidly when oxygen is present. Rennet is an example of a third type, the activity of which is not impaired by visible rays, but is rapidly destroyed by ultra-violet radiation in a vacuum. W. O. W.

The Mode of Action of Phosphatese. A. VON LEBEDEFF (*Zeitsch. physiol. Chem.*, 1911, **75**, 499—500).—Polemical against Euler and Kullberg (Abstr., 1911, i, 1057). The results obtained by these authors were vitiated by the use of impure yeast-extract.

H. B. H.

The Influence of Temperature on the Action of Phosphatese. HANS VON EULER and HJALMAR OHLSÉN (*Biochem. Zeitsch.*, 1911, **37**, 312—320).—The aqueous extract of yeast dried at 50° does not produce a synthesis of phosphoric esters of sugars from dextrose and phosphoric acid unless the former substance is previously partly fermented with living yeast. A synthetical enzyme can therefore be separated from other enzymes in yeast. The extract of dried yeast becomes more active synthetically if it is warmed to 40° before acting on the mixture of phosphate and partly fermented dextrose. The explanation of this phenomenon has not yet been found, but preliminary experiments indicate that it is not due to the destruction of inhibitory substances. S. B. S.

5-Nitro-2-aminophenylarsinic Acid. LUDWIG BENDA (*Ber.*, 1911, **44**, 3293—3297).—It has been shown previously (Abstr., 1908, i, 591) that in the preparation of aminoarylarsinic acids from aromatic amines, the arsenic always enters the para-position to the amino-group, provided that this position is unoccupied. In the case of para-substituted amines, either the introduction of arsenic cannot be effected, or exceedingly small yields of *o*-aminoarylarsinic acids are obtained (Benda, Abstr., 1908, i, 747). An exception to this rule has been found in *p*-nitroaniline, which is readily converted into 5-*nitro*-2-*aminophenylarsinic acid*, $NO_2 \cdot C_6H_3(OH) \cdot AsO(OH)_2$, by heating it with arsenic acid at 210°. The acid crystallises in lustrous, orange-yellow prisms, m. p. 235—236° (decomp.), and yields an *acetyl* derivative and an almost colourless *diazo*-compound. The constitution of the acid has been established by its conversion into 2-iodo-4-nitroaniline (Michael and Norton, Abstr., 1878, 406) by the action af potassium iodide and sulphuric acid on the aqueous solution of its sodium salt.

When heated with aqueous sodium hydroxide, it yields 5-*nitro-2-hydroxyphenylarsinic acid*, $NO_2\cdot C_6H_3(OH)\cdot AsO(OH)_2$. This forms stout, lustrous, pale amber-yellow crystals, m. p. 247—248° (decomp.), and yields a *monopotassium* salt, $C_6H_5O_6NKAs,H_2O$, crystallising in almost colourless needles or leaflets; the *dipotassium* salt forms intensely yellow, felted needles.

3 : 5-*Dinitro-2-hydroxyphenylarsinic acid*,

$$OH\cdot C_6H_2(NO_2)_2\cdot AsO(OH)_2,$$

prepared by nitrating the mononitro-acid, crystallises in pale yellow needles, m. p. 237°.

Reduction of 5-nitro-2-hydroxyphenylarsinic acid by means of sodium hyposulphite yields 5 : 5′-*diamino*-2 : 2′-*dihydroxyarsenobenzene*, which forms a yellow powder, yields a microcrystalline *dihydrochloride*, and, when oxidised with sodium hypochlorite in alkaline solution in the presence of *p*-xylenol, gives a cornflower-blue solution of the corresponding *indophenolarsinic acid*. F. B.

Constitution of the Isomeric Aminophenylarsinic Acids, and of Michaelis's Nitrophenylarsinic Acid. ALFRED BERTHEIM and LUDWIG BENDA (*Ber.*, 1911, **44**, 3297—3300).—*m*-Aminophenylarsinic acid has been prepared by eliminating the amino-group from 3-nitro-4-aminophenylarsinic acid (Abstr., 1911, i, 1055) and 5-nitro-2-aminophenylarsinic acid (preceding abstract), and found to be identical with the acid previously obtained (Bertheim, Abstr., 1908, i, 590) by the reduction of the nitrophenylarsinic acid prepared by Michaelis and Loesner (Abstr., 1894, i, 187) by directly nitrating phenylarsinic acid. Michaelis and Loesner's acid is accordingly *m*-nitrophenylarsinic acid.

The elimination of the amino-group from 3-nitro-4-aminophenylarsinic acid was accomplished by diazotisation and subsequent treatment of the resulting diazo-compound with hypophosphorous acid. In the case of 5-nitro-2-aminophenylarsinic acid, the replacement of the diazo-group was effected by means of copper bronze and alcohol. The *m*-nitrophenylarsinic acid thus obtained was isolated by means of the *zinc* salt, and reduced with sodium amalgam to *m*-aminophenylarsinic acid. F. B.

***p*-Phenylenediaminearsinic Acid.** LUDWIG BENDA (*Ber.*, 1911, **44**, 3300—3304). — p-*Phenylenediaminearsinic* [2 : 5-*diaminophenylarsinic*] *acid* is prepared by reducing 5-nitro-2-aminophenylarsinic acid (preceding abstracts) in aqueous sodium hydroxide solution with ferrous chloride. It crystallises in slender needles, which become violet on exposure to air and light, and decompose at 210—215°. It reacts with only one molecule of nitrous acid to form a *diazo*-compound, which yields reddish-violet, yellowish-orange, and red *azo*-dyes with *R*-salt, resorcinol, and β-naphthol respectively. When the *diazo*-compound is treated with copper and alcohol, and the resulting mono-aminophenylarsinic acid again diazotised and coupled with β-naphthol, a red *azo*-dye is obtained, which is reduced by sodium hyposulphite to *m*-aminophenylarsinic acid. The diazotisation of 2 : 5-diaminophenylarsinic acid therefore takes places at the amino-group in the 2-position.

Attempts to prepare *o*-aminophenylarsinic acid (see following abstract) by acetylating 2 : 5-diaminophenylarsinic acid, diazotising the resulting 2-*amino*-5-*acetylaminophenylarsinic acid*, and combining the *diazo*-compound thus obtained with β-naphthol, followed by hydrolysis and subsequent removal of the amino-group from the resulting *azo*-dye, were only partly successful. *o*-Aminophenylarsinic acid was identified in the product, but could not be isolated in a crystalline condition. F. B.

o-Aminophenylarsinic (o-Arsanilic) Acid. LUDWIG BENDA (*Ber.*, 1911, **44**, 3304—3308).—5-Nitro-2-aminophenylarsinic acid (preceding abstracts) and oxalic acid react when heated with concentrated aqueous sodium hydroxide at 160—165° to form 4 : 4′-*dinitro-oxanilide*-2 : 2′-*diarsinic acid*,

$$AsO(OH)_2{\cdot}C_6H_3(NO_2){\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_6H_3(NO_2){\cdot}AsO(OH)_2,$$

which is reduced by iron and acetic acid to 4 : 4′-*diamino-oxanilide*-2 : 2′-*diarsinic acid*. The amino-group is eliminated from the latter compound by diazotisation and treatment of the resulting *diazo*-compound with copper and alcohol.

The *oxanilide*-2 : 2′-*diarsinic acid*,

$$AsO(OH)_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)_2,$$

thus obtained crystallises in lustrous, silvery leaflets, and is hydrolysed by dilute sulphuric acid to o-*aminophenylarsinic acid*,

$$NH_2{\cdot}C_6H_4{\cdot}AsO(OH)_2.$$

This crystallises in needles, m. p. 153°, and is distinguished from its isomerides by its much greater solubility in water and the ease with which the arsenic acid residue is removed. When heated with potassium iodide and dilute sulphuric acid at 80°, it is instantly converted into *o*-iodoaniline. Its toxicity is much greater than that of the *p*-isomeride. The crystalline *barium* and *silver* salts are described. F. B.

Nitrohydroxyarylarsinic Acids. LUDWIG BENDA and ALFRED BERTHEIM (*Ber.*, 1911, **44**, 3445—3448).—The nitration of *p*-hydroxyphenylarsinic acid and of 4-hydroxy-5-methylarsinic acid has been studied.

3 - *Nitro* - 4 - *hydroxyphenylarsinic acid* is formed when sodium *p*-hydroxyphenylarsinate dissolved in concentrated sulphuric acid is treated with the theoretical quantity of nitric acid (D 1·4), the temperature not being allowed to rise above 0°. It forms nearly white crystals, which decompose when heated. The *mono*-, *di*-, and *tri-sodium* salts were prepared, the last-named existing in two forms. Its p-*toluenesulphonic* ester, colourless leaflets, m. p. 171° previously sintering, was also investigated.

3 : 5-*Dinitro*-4-*hydroxyphenylarsinic acid* was prepared by nitrating sodium *p*-hydroxyphenylarsinate dissolved in concentrated sulphuric acid by means of nitric acid (D 1·52), the temperature being maintained at between 15° and 20°. It decomposes when heated. In alkaline solution it yields a deep red coloration on the addition of sodium thiosulphate. The mononitro-acid shows no change in colour on similar treatment.

5-*Nitro*-6-*hydroxy*-m-*tolylarsinic acid* was prepared from 4-hydroxy-*m*-tolylarsinic acid according to the method used in the preparation

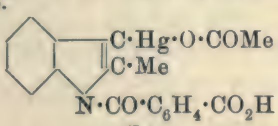
of 3-nitro-4-hydroxyphenylarsinic acid. It crystallises from 50% acetic acid in faintly yellow leaflets or needles. H. W.

3-Nitro-4-hydroxyphenylarsinic Acid. LUDWIG BENDA (*Ber.*, 1911, **44**, 3449—3451).—Difficulties were encountered in applying the method given in the previous abstract to the technical preparation of 3-nitro-4-hydroxyphenylarsinic acid, the latter being required for the preparation of the drug salvarsan. Attempts were therefore made to prepare an azo-compound from crude *p*-hydroxyphenylarsinic acid, which, on reduction, would yield either 3-amino-4-hydroxyphenylarsinic acid or di-*m*-aminodi-*p*-hydroxyarsenobenzene (the base of salvarsan). The compounds obtained by coupling *p*-hydroxyphenylarsinic acid with *p*-nitrodiazobenzene or with diazobenzene were, however, found to be completely free from arsenic.

3-Nitro-4-hydroxyphenylarsinic acid was finally obtained in quantitative yield by warming 3-nitro-4-aminophenylarsinic acid (compare Bertheim, Abstr., 1911, i, 1035) with potassium hydroxide and subsequent treatment with hydrochloric acid. When similarly treated, 5-nitro-6-amino-*m*-tolylarsinic acid yielded the corresponding 5-nitro-6-hydroxy-*m*-tolylarsinic acid. H. W.

Preparation of Mercury Derivatives of Indoles. C. F. BOEHRINGER & SÖHNE (D.R.-P. 236893).—The action of mercuric acetate on indole derivatives in alcoholic solution yields products which are readily decomposed by hot dilute mineral acids into their generators.

The following *compounds* were prepared: (I) $C_{19}H_{15}O_5NHg$ (a red precipitate) from phthalylmethylindole; (II) $C_{11}H_{11}O_2NHg$ (needles) from 1-methylindole; (III) $C_{10}H_9O_3NHg$ from 1-methylindolecarboxylic acid; (IV) $C_{15}H_{13}O_2NHg$ (a brown precipitate) from *anisylindole*, m. p. 226°, obtained by the action of zinc chloride on acetylanisolephenylhydrazone; (V) $C_{22}H_{24}O_6N_2Hg_3$ (a yellow precipitate) from 2-methylindole.



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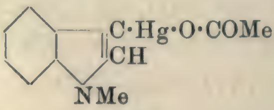

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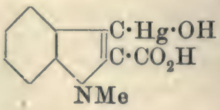

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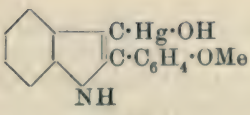

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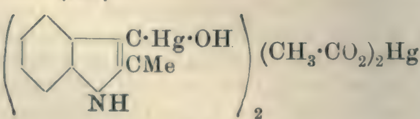


(V.)

F. M. G. M.

Organic Chemistry.

Three Normal Saturated Hydrocarbons: Triacontane, Tetratriacontane, and Hexatriacontane. ALBERT GASCARD (*Compt. rend.*, 1912, **154**, 1484—1487).—Pentadecyl alcohol (Simonini, Abstr., 1892, 1301) was converted into *pentadecyl iodide*, brilliant scales, m. p. 24·5°. This was boiled with xylene and sodium for twelve hours, when n-*triacontane*, $C_{30}H_{62}$, was obtained as brilliant scales, m. p. 65·2—65·5°, isomeric, if not identical, with the hydrocarbons isolated from plants by Klobb (Abstr., 1910, ii, 1100), and from the products of electrolysis of potassium palmitate by Petersen (Abstr., 1906, i, 331).

Heptadecyl stearate was prepared by heating silver stearate with iodine. The compound crystallises in silky lamellæ, m. p. 64·7°, and on hydrolysis yields n-*heptadecyl alcohol*, pearly scales, m. p. 54°. *Heptadecyl iodide*, brilliant lamellæ, m. p. 33·6°, when treated with sodium gives n-*tetratriacontane*, $C_{34}H_{70}$, occurring as very brilliant scales, m. p. 73·2°.

Similarly, *octadecyl iodide*, m. p. 33·5°, has been converted into n-*hexatriacontane*, $C_{36}H_{74}$, a substance crystallising in brilliant lamellæ, m. p. 76°. W. O. W.

Catalytic Action. V. Friedel and Crafts' Reaction. JACOB BÖESEKEN (*Rec. trav. chim.*, 1911, **30**, 381—391. Compare Abstr., 1910, i, 152).—In continuation of the previous work it is shown that dissociable chlorides, such as sulphuryl chloride, pentachloroethane, and chloral, act as a mixture of the non-decomposed molecule, in which the chlorine atoms are activated, and of its products of decomposition. The first-named chloride has been tried with benzene, toluene, and anisole. With the two former the products of reaction are those of the condensation of the non-dissociated molecule as well as those of the products of dissociation. The latter are in excess, since the equilibrium $SO_2Cl_2 \rightleftarrows SO_2 + Cl_2$ is displaced to the right by the catalyst. In the case of anisole the reaction only yields the substances formed from the products of dissociation, probably owing to the fact that the anisole is attacked so energetically by these products.

With pentachloroethane, it is only the activated chlorine in the undecomposed molecule which attacks benzene, although at the same time some of the pentachloroethane is decomposed into tetrachloroethylene and hydrogen chloride.

Chloral and benzene give a very complex reaction, a large number of substances being formed, owing to the fact that the products of decomposition of the chloral can re-combine to form other substances. W. G.

Autoxidation of Trichloroethylene. ERNST ERDMANN (*J. pr. Chem.*, 1912, [ii], **85**, 78—89).—Trichloroethylene was prepared by

the action of alcoholic potash on tetrachloroethane; it has b. p. 85·8—86·0°/741·6 mm., m. p. −83°, D_4^{20} 1·4649, D_4^{15} 1·4695.

In contact with air this liquid undergoes autoxidation; at elevated temperatures and increased pressure, for example, in an autoclave, the reactions are complex, a mixture of halogen compounds boiling between 100 and 240° being obtained, due to polymerisations and secondary actions; at the ordinary pressure and below 60° the process is much simpler, the final products being hydrogen chloride, carbon monoxide, carbonyl chloride, and dichloroacetyl chloride, the latter being the only liquid product. In order to obtain measurable quantities of the products the experiment may have to extend over several weeks; the rate of reaction varies as the ratio of trichloroethylene to oxygen. With excess of oxygen, after twenty-eight days, the amount of oxygen removed is between 1 and 2 atoms for each molecule of trichloroethylene originally present, thus indicating the simultaneous reactions: $CHCl{:}CCl_2 + O = CHCl_2{\cdot}COCl$ and $CHCl{:}CCl_2 + O_2 = CO + HCl + COCl_2$.

On passing ozonised oxygen through trichloroethylene, hydrogen chloride, carbonyl chloride, and carbon monoxide are formed, but no dichloroacetyl chloride. By using a solution of trichloroethylene in hexahydrotoluene at −79°, the increase in weight due to ozonide formation could be directly determined and indicated an addition of one molecule of ozone to each molecule of trichloroethylene; the ozonide, which was too unstable and explosive to be examined in a pure state, is therefore formulated $\begin{array}{l}\mathrm{CHCl{\cdot}CCl_2}\\ \;\vert\qquad\;\;\vert\\ \mathrm{O{-\!-\!-}O{:}O}\end{array}$. The gases from an explosion of the ozonide contained carbon monoxide, carbonyl chloride, hydrogen chloride, and an oxide of chlorine; the decomposition can be moderated by solution in chloroform or hexahydrotoluene, but the products are the same with the exclusion of the oxide of chlorine. In decomposition in the presence of water, hydrogen peroxide is formed. The spontaneous decomposition of the ozonide in a dilute solution (for example, excess of trichloroethylene), in the absence of water, indicates that an atom of oxygen is first removed, being chemically absorbed by the solvent, and after removal of excess of trichloroethylene in a vacuum, a pungent *oil* remains, to which is attributed the formula $\begin{array}{l}\mathrm{CHCl{\cdot}CCl_2}\\ \;\vert\qquad\;\;\vert\\ \mathrm{O{-\!-\!-\!-}O}\end{array}$; it rapidly decomposes, giving carbon monoxide, hydrogen chloride, and carbonyl chloride, the first two of which can be regarded as the decomposition products of the intermediate formyl chloride. No indication of dichloroacetyl chloride was detected in any decomposition of the ozonide.

The author, therefore, suggests an explanation of the autoxidation of trichloroethylene described by the formulæ:

$$\begin{array}{ccccccc}
\mathrm{CHCl{:}CCl_2} & \longrightarrow & \mathrm{CHCl{\cdot}CCl_2} & \longrightarrow & \mathrm{CHCl{\cdot}CCl_2} & \longrightarrow & \mathrm{CHCl_2{\cdot}COCl.} \\
 & & \diagdown\mathrm{O}\diagup & & \diagdown\mathrm{O}\diagup & & \\
 & & \ddot{\mathrm{O}} & & +\mathrm{O} & & \\
\text{(I.)} & & \text{(II.)} & & \text{(III.)} & & \text{(IV.)}
\end{array}$$

The method of formation of the dichloroacetyl chloride is thus explained. The nascent oxygen formed at (III), together with ordinary

oxygen, then attacks another molecule of trichloroethylene, like a molecule of ozone, giving the ozonide, which then decomposes as described above.

The possibility of autoxidation is not restricted to unsymmetrical substituted ethylenes (compare Demole, Abstr., 1878, 847; Demole and Dürr, Abstr., 1878, 846; Anschütz, Abstr., 1880, 98).

The action of other oxidising agents on trichloroethylene was also investigated; anhydrous ferric chloride attacks the substance in a sealed tube first at 85°, the former being reduced to the ferrous salt, whilst the latter gives pentachloroethane; at higher temperatures the last substance loses a molecule of hydrogen chloride, and the resultant tetrachloroethylene becomes further converted into hexachloroethane.

D. F. T.

The Distillation of Methyl Alcohol. Gustav Birstein, H. Denneler, and Alfred Heiduschka (*Zeitsch. angew. Chem.*, 1911, **24**, 2429—2430).—Two series of experiments on the volatility of solutions of methyl alcohol have been carried out. In the first series, in which the solutions were distilled under constant pressure, it was shown that even dilute solutions of methyl alcohol yielded distillates comparatively rich in methyl alcohol. In the second series, in which the temperature was kept approximately constant, and air drawn through the solution, the concentration of alcohol in the distillate was found to be invariably slightly greater than in the original solution. The bearing of these results on the commercial preparation of formaldehyde is discussed.

H. W.

Action of Potassium Hydroxide on Primary Alcohols; Preparation of the Corresponding Acids. Marcel Guerbet (*Compt. rend.*, 1912, **154**, 1487—1489; *J. Pharm. Chim.*, 1912, [vii], **5**, 58—64).—Dumas and Stas (*Ann. Chim. Phys.*, 1840, [2], **73**, 113) found that potassium hydroxide acts on methyl, ethyl, and amyl alcohols at 200—230°, transforming them into the corresponding acids, with liberation of hydrogen. It is now shown that in the case of the lower alcohols, dehydration also occurs with formation of ethylenic hydrocarbons. The higher alcohols, however, form only hydrogen and the potassium salt of the acid. This method of oxidation is very advantageons for alcohols above the C_6 terms, since it is unnecessary to employ sealed tubes, and the yield is practically theoretical.

β-Methylpentanol gives a 95% yield of the corresponding acid, which was characterised by conversion into its *amide*, m. p. 85°. *β-Heptylhexoamide*, $CH_3\cdot[CH_2]_3\cdot CH(C_7H_{15})\cdot CH_2\cdot CO\cdot NH_2$, has m. p. 108°.

W. O. W.

Calcium Ethoxides. Robert de Forcrand (*Compt. rend.*, 1912, **154**, 1441—1444. Compare Abstr., 1895, i, 259; Doby, Abstr., 1903, i, 546; Chablay, this vol., i, 3).—Calcium ethoxide,

$$Ca(OEt)_2,2EtOH,$$

when allowed to remain over concentrated sulphuric acid, slowly loses alcohol. A specimen prepared in 1905 now approximates in com-

position to the formula $3CaO,EtOH,2H_2O$ or $Ca(OEt)_2,5CaO,5H_2O$. The suggestion is put forward that a process of catalytic decomposition occurs, calcium oxide, the active agent, behaving as the thorium dioxide in Sabatier and Mailhe's experiments (Abstr., 1910, i, 294). Calcium ethoxide is analogous to the hypothetical compound $ThO(OEt)_2$, losing ethylene or ether like this substance, but having greater stability at the ordinary temperature. W. O. W.

The Crystallographic Distinctions of Nitroglycerol. SIGURD NAUCKHOFF (*Zeitsch. Scheiss. Sprengstoffw.*, 1911, 6, 124—125).—The paper contains sketches and measurements of two forms of nitroglycerol crystals; they are of the bipyramidal class of the rhombic system, but when obtained from supercooled nitroglycerol have a flattened, tabular habit, whilst those deposited from saturated ethereal solution are of rhombic character; their optical properties are also described.

The author discusses the work of Kast (*Atti VI Cong. Internaz. chim. appl. IIIb*), and considers that the m. p. of nitroglycerol is $-12.5°$, instead of $-13.5°$ (Kast). F. M. G. M.

Transformations of Thio- and Seleno-phosphoric Esters. P. PISTSCHIMUKA (*J. pr. Chem.*, 1911, [ii], 84, 746—760; from *Mem. Inst. agr. forest., Nowo Alexandria,* 1911, 1—148).—The esters of thiophosphoric acid should exist in two isomeric forms, $PO(OR)_2 \cdot SR$ and $PS(OR)_3$, but, hitherto, only the latter series have been prepared. It is found that the esters of this series combine with a large number of metallic salts, yielding additive compounds, which undergo decomposition, either at the ordinary temperature or when heated, with the formation of derivatives of *iso*thiophosphoric acid, $PO(OH)_2 \cdot SH$; thus, the additive compounds of the alkyl esters with silver nitrate, $PS(OR)_3,AgNO_3$, readily lose one molecule of alkyl nitrate and form salts of the composition $PO(OR)_2 \cdot SAg$. The isomeric esters are obtained from these salts by the action of alkyl iodides.

A similar transformation into derivatives of the isomeric acid is caused by alkalis, alkyloxides, alkyl halides, and ammonia, although the formation of intermediate additive products with these compounds could not be observed. The transformation is, however, not confined to esters of monothiophosphoric acid, but is common to all esters of the type $PS(XR)_2 \cdot OR$ (where $X = O$ or S), derivatives of $PO(XH)_2 \cdot SH$ being produced.

Esters of selenophosphoric acid, $PSe(OR)_3$, have also been prepared and converted into the isomeric forms by methods similar to those employed in the case of the thiophosphates.

The alkyl thiophosphates of the type $PS(OR)_3$ were prepared by the method described previously (Abstr., 1909, i, 5); the ethyl ester has b. p. 106°/20 mm., D_0^0 1·0944; the *propyl* ester, b. p. 133—134°/20 mm., D_0^0 1·0409; the iso*butyl* ester, b. p. 155°/20 mm., D_0^0 0·9907. On treatment with nitric acid, they yield esters of phosphoric acid, and are converted by sodium into the corresponding alkyl phosphites.

The *compound*, $PSCl_2 \cdot SEt$, obtained by heating the acid chloride,

$PCl_2\cdot SEt$, with sulphur, has b. p. 92°/10 mm., D_0^0 1·4453; it reacts with sodium ethoxide, yielding *ethyl dithiophosphate*, $PS(OEt)_2\cdot SEt$, b. p. 130°/20 mm., D_0^0 1·1340.

Ethyl trithiophosphate, obtained from the chloride $PSCl_2\cdot OEt$ and sodium ethylmercaptide, is a liquid, b. p. 155°/20 mm., D_0^0 1·1716.

The following *additive* compounds with mercuric chloride were prepared: $PS(OMe)_3,2HgCl_2$, transparent needles, melting at 102°, and simultaneously losing methyl chloride, forming the *compound*, $PO(OMe)_2\cdot SHgCl,HgCl_2$, which passes at 150° into the *compound*, $SHgCl\cdot PO(OMe)\cdot OHgCl$; $SHgCl\cdot PO(OEt)_2,HgCl_2$, forms stout, transparent prisms, m. p. 66°, which at 85° yield the *compound*,

$SHgCl\cdot PO(OEt)\cdot OHgCl$;

$PS(OPr^{\alpha})_3,2HgCl_2$; $PS(OCH_2Pr^{\beta})_3,2HgCl_2$; $PS(SEt)_2\cdot OEt,2HgCl_2$, white needles, m. p. 81°; $PS(SEt)_3,2HgCl_2$, m. p. 84°. All additive compounds of the type $PS(XR)_2\cdot OR,2HgCl_2$ lose one molecule of alkyl chloride at a relatively low temperature.

The esters of thiophosphoric acid form with ferric chloride *additive* compounds of the general formula $3PS(OR)_3,2FeCl_3$, which lose three molecules of alkyl chloride when heated; the *methyl* compound forms large, yellow prisms, m. p. 125°; the *ethyl* compound is crystalline; the *propyl* and iso*butyl* compounds are oils.

The ethyl esters of di- and tri-thiophosphoric acid yield with ferric chloride oily *additive* compounds having a similar composition. Compounds of the same type are formed with ferric bromide, but only the *methyl* compound, $3PS(OMe)_3,2FeBr_3$, m. p. 99°, is crystalline.

Ethyl thiophosphate combines with platinic chloride, yielding the *compound*, $3PS(OEt)_3,2PtCl_4$, orange-yellow needles, m. p. 103°. The crystalline *compound* of methyl thiophosphate and auric chloride has m. p. 110°.

Silver nitrate dissolves in methyl thiophosphate, yielding methyl nitrate and the *silver* salt, $PO(OMe)_2\cdot SAg$, and in ethyl thiophosphate to form the *additive* compound, $PS(OEt)_3,AgNO_3$, which decomposes slowly at the ordinary temperature into ethyl nitrate and the *silver* salt, $PO(OEt)_2\cdot SAg$, m. p. 82°.

Similar *compounds* are formed by the propyl and *iso*butyl esters. The phenyl ester reacts with silver nitrate, yielding *o*-nitrophenol and the *compound*, $PO(OPh)_2\cdot SAg$. The behaviour of silver nitrite resembles that of the nitrate.

Mercuric iodide combines with the alkyl thiophosphates, $PS(OR)_3$, to form additive compounds, which are derivatives of the isomeric ester, $PO(OR)_2\cdot SR$. Thus, ethyl thiophosphate, when heated with mercuric iodide at 180°, yields the *compound*, $PO(OEt)_2\cdot SEt,2HgI_2$.

Similar compounds are formed by the esters of di- and tri-thiophosphoric acid. The interaction of alcoholic ammonia and ethyl thiophosphate yields ethylamine and the *compound*, $NH_2\cdot PO(OEt)_2$.

Sodium hydroxide, sodium ethylmercaptide, and sodium alkyloxides react with the alkyl thiophosphates to form sodium salts of the composition $PO(OR)_2\cdot SNa$. The action of sodium hydroxide and sodium alkyloxides on the esters of di- and tri-thiophosphoric acids leads to the formation of a mercaptan or alkyl sulphide, together

with sodium salts containing a smaller number of atoms in the molecule. Sodium ethylmercaptide, on the other hand, gives rise to the *sodium* salts, $SNa\cdot PO(SEt)\cdot OEt$ and $PO(SEt)_2\cdot SNa$.

The isomeric thiophosphoric esters of the type $PO(OR)_2\cdot SR$ are obtained by the action of alkyl iodide on the above-mentioned silver salts, $PO(OR)_2\cdot SAg$, in alcoholic solution. The methyl ester has b. p. 107°/20 mm., D_0^0 1·2685; the *ethyl* ester, b. p. 122°/20 mm., D_0^0 1·1245; the *propyl* ester, b. p. 156°/20 mm., D_0^0 1·0532; the iso*butyl* ester, b. p. 170°/20 mm., D_0^0 1·0102.

The esters of selenophosphoric acid of the formula $PSe(OR)_3$ are formed by the combination of "molecular" selenium and esters of phosphorous acid; the *methyl* ester is a liquid, b. p. 95°/20 mm., D_0^0 1·5387; the *ethyl* ester has b. p. 117°/20 mm., D_0^0 1·3189.

The following *additive* compounds were prepared: $PSe(OMe)_3,HgCl_2$; $PSe(OEt)_3,HgCl_2$; $PSe(OMe)_3,HgI_2$, m. p. 66°, and is simultaneously transformed into its *isomeride*, $PO(OMe)_2\cdot SeMe,HgI_2$; $PSe(OEt)_3,HgI_2$, large, yellow prisms, m. p. 32°, which pass at 75° into the *isomeride*, $PO(OEt)_2\cdot SeEt,HgI_2$, m. p. 95°, and when warmed under diminished pressure lose ethyl iodide, yielding the *compound*, $PO(OEt)_2\cdot SeHgI$.

Ethyl selenophosphate and sodium ethyl mercaptide react to form the *sodium* salt, $PO(OEt)_2\cdot SeNa$, m. p. 196°; the corresponding *lead* salt is unstable, and yields with ethyl iodide the *ester*, $PO(OEt)_2\cdot SeEt$, a liquid, b. p. 140°/20 mm., D_0^0 1·3593.

Esters of the type $PS(XR)_2\cdot OR$ are transformed by prolonged heating with an excess of alkyl iodide into their isomerides. Thus, ethyl thiophosphate, $PS(OEt)_3$, is converted by ethyl iodide into its isomeride, $PO(OEt)_2\cdot SEt$, and by *iso*butyl iodide into the *ester*, $PO(OEt)_2\cdot S\cdot CH_2Pr^{\beta}$.

With respect to the mechanism of the above-mentioned transformations the author considers that, in all cases, additive compounds containing either a quadrivalent or sexavalent sulphur or selenium atom are first produced, and that these subsequently undergo tautomeric change and decomposition; the action of sodium ethoxide on ethyl dithiophosphate is represented as follows:

$$PS(OEt)_2\cdot SEt \xrightarrow{NaOEt} NaS\cdot S(OEt)\colon P(OEt)_2\cdot SEt \longrightarrow$$
$$NaS\cdot S\cdot P(OEt)_3\cdot SEt \longrightarrow NaS\cdot PO(OEt)_2 + Et_2S.$$

F. B.

Complex Compounds of Platinous Bromide with Organic Sulphides. LEO A. TSCHUGAEFF and (Mlle.) D. FRAENKEL (*Compt. rend.*, 1912, **154**, 33—35. Compare Abstr., 1910, i, 354).—When an aqueous solution of potassium platinobromide is treated with ethylenedithioglycol ether, the *compound*, $[Pt2C_2H_4(SEt)_2]PtBr_4$, separates as a grey, microcrystalline precipitate, m. p. 157°. At 100° this substance changes into a yellow isomeride having the same m. p., but a greater solubility in water and chloroform. The above constitution is assigned to the substance on the ground that it unites with Reiset's bromide, forming the salt, $[Pt4NH_3]PtBr_4$, together with a yellow *compound*, m. p. 157—158°. The latter has the constitution $[C_2H_4(SEt)_2]_2PtBr_2$, since it can also be prepared by mixing the grey salt with ethylenedi-

thioglycol ether and potassium platinobromide in equimolecular proportions.

Potassium platinobromide reacts with methyl sulphide, giving an unstable grey compound, $[Pt4Me_2S]PtBr_4$, m. p. 160°. On crystallisation from chloroform this changes into Blomstrand's salt, $(Me_2S)_2PtBr_2$.

Platinoiodides do not form derivatives with organic sulphides.

W. O. W.

Intramolecular Rearrangements of Aliphatic Sulphoxides. THOMAS P. HILDITCH (*Ber.*, 1911, **44**, 3583—3589).—By treatment with alcoholic hydrogen chloride or with boiling acetic anhydride, di*iso*amylsulphoxide is converted into *iso*amyl mercaptan and *iso*valeraldehyde; by the former reagent, thionyldiacetic acid is decomposed into thioglycollic and glyoxylic acids. *a-Thionyldi*isobutyric *acid*,

$$SO(CMe_2\cdot CO_2H)_2,$$

m. p. 186°, is unchanged by alcoholic hydrogen chloride.

An explanation of these decompositions is given which assumes the intermediate formation of thionium compounds. C. S.

Complex Compounds of Platinum with Organic Selenides. I. E. FRITZMANN (*Zeitsch. anorg. Chem.*, 1911, **73**, 239—255).—The isomerism of the compounds of platinous chloride with organic sulphides has been discussed by Tschugaeff and Subbotin (Abstr., 1910, i, 354). The corresponding selenium compounds have not been examined, with the exception of those derived from ethyl selenide (Petren, *Zeitsch. anorg. Chem.*, 1899, **20**, 62).

The isomerism observed is similar to that of the sulphur compounds. The α-compounds are more soluble than the β-compounds, and are darker in colour. The former are to be regarded, in accordance with Werner's views, as *cis*-modifications, and the latter as *trans*-modifications. The γ-compounds are less stable than those of sulphur.

A 4% solution of potassium platinochloride (1 mol.) is shaken with the alkyl selenide (2 mols.) until decolorised. The α-compound is then chiefly obtained. In order to prepare the β-compound, 4 mols. of selenide are used, and the mixture is digested at 70—75° in a closed vessel until all is dissolved. The cooled solution is evaporated in a vacuum over calcium chloride and solid paraffin or rubber, and potassium chloride is then removed by washing. For analysis, the compound is decomposed with sulphuric acid, and heated in hydrogen to remove selenium, the residual platinum being weighed. Selenium is estimated by boiling with aqua regia in a quartz vessel, evaporating, and precipitating the slightly acid solution with a hot saturated solution of hydrazine sulphate. The precipitated mixture of platinum and selenium is collected, dried at 100°, and weighed, and the selenium is then removed by heating in hydrogen.

Methyl selenide platinous chloride, $PtCl_2,2Me_2Se$, has m. p. 163—163·5°. The α-form is partly converted into the β-form by repeated crystallisation from chloroform, and the reverse change is also observed. At a

low temperature it is possible to obtained the γ-modification, but it can only be isolated in the form of the green Magnus salt,

$$(Pt,4Me_2Se)Cl_2,$$

by the addition of a solution of Reiset's salt, $(Pt,4NH_3)Cl_2$.

Methyl selenide platinous bromide, $PtBr_2,2Me_2Se$, is red, and has m. p. 171° (decomp.). Propyl selenide forms the *compound*, $PtCl_2,2Pr_2Se$, m. p. 42·5—43°; only the α-modification has been obtained. *n*-Butyl selenide only yields an oily product. *iso*Amyl selenide yields an *α-compound*, $PtCl_2,2(C_5H_{11})_2Se$, m. p. 97—97·5°, and a *β-compound*, m. p. 115—116°. The phenyl selenide *α-compound* has m. p. 180°, and the *β-compound*, m. p. 178—179°.

Diethyl trimethylene diselenide forms an α- and a *β-compound*, $2PtCl_2,2CH_2(CH_2{\cdot}SeEt)_2$, both of which have m. p. 176—176·5°. A γ-modification has been recognised by conversion into the Magnus salt. C. H. D.

Chemico-crystallographic Notes. L. WAGNER (*Zeitsch. Kryst. Min.*, 1911, **50**, 47—56).—Phosphonium iodide, PH_4I; tetragonal, D 2·860. Tetramethylphosphonium iodide; tetragonal, $a:c = 1:0·7310$, D 1·746. Calcium formate, $Ca(CHO_2)_2$; orthorhombic (bipyramidal) [$a:b:c = 0·7599:1:0·9363$ (Plathan)], D 2·023. Strontium formate, $Sr(CHO_2)_2$; orthorhombic (bisphenoidal), $a:b:c = 0·7846:1:0·8292$, D 2·693. Mixed crystals of calcium and strontium formate resemble those of either one or other of the simple salts, but they also show an intermediate tetragonal form; the two salts are therefore isotrimorphous. Strontium formate forms the hydrate, $Sr(CHO_2)_2,2H_2O$, D 2·259; but calcium formate forms no hydrate. Anhydrous oxalic acid; orthorhombic, $a:b:c = 0·8301:1:0·7678$, D 1·900. Nitrobenzene; monoclinic (domatic?), $a:b:c = 1·280:1:?$; $\beta = 117°21'$, m. p. 3·8°.

L. J. S.

Direct Synthesis of the Glycerides. GIUSEPPE GIANOLI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 653—654. Compare Abstr., 1911, i, 349; Bellucci and Manzetti, *ibid.*, i, 259).—Polemical.

R. V. S.

Formation of Cork. MAX VON SCHMIDT (*J. pr. Chem.*, 1911, [ii], **84**, 830—832).—A reply to Zeisel's criticism (Abstr., 1911, i, 768) of previous work of the author (Abstr., 1910, i, 540). F. B.

Derivatives of Tetrolaldehyde and its Acetal [Diethoxybutinene]. PAUL L. VIGUIER (*Compt. rend.*, 1911, **153**, 1231—1233. Compare Abstr., 1909, i, 691).—On treating diethoxybutinene with aniline hydrochloride, the *hydrochloride*,

$$NHPh{\cdot}CMe{:}CH{\cdot}CH{:}NPh,HCl,$$

is obtained as yellow crystals decomposing at 160°. No definite compound was obtained from aniline, and phenylmethylpyrazole was the only definite product with phenylhydrazine. Urethane combines with the acetal, in presence of hydrogen chloride, giving the compound, $CMe{\vdots}C{\cdot}CH(NH{\cdot}CO_2Et)_2$, slender needles, m. p. 188—189°. The acetal unites with alcohol, in presence of sodium ethoxide, forming

*αα*γ*-triethoxy-*Δ^{β}*-butylene*, OEt·CMe:CH·CH(OEt)$_2$, b. p. 190—195°, under ordinary pressure, 82—86°/15 mm., D^{21} 0·908, n_D^{21} 1·430.

Exposure to air converts triethoxybutylene into β-ethoxycrotonic acid. On hydrolysis, it appears to form acetoacetaldehyde, but this rapidly polymerises to triacetylbenzene. When treated with semicarbazide hydrochloride, it yields a *compound*, m. p. 127—128°, having the constitution $\begin{matrix}\text{CH:CMe}\\ | \\ \text{CH}=\!=\text{N}\end{matrix}\!>\!\text{N·CO·NH}_2$. W. O. W.

Action of Monochlorocarbamide on Ketones. AUGUSTE BÉHAL and A. DETŒUF (*Compt. rend.*, 1911, **153**, 1229—1231. Compare Abstr., 1911, i, 957).—On allowing chlorocarbamide to act on the calculated amount of an aliphatic ketone in aqueous solutions for three to five days, an excellent yield of a monochloro-ketone is obtained. Symmetrical ketones give the halogen derivative, in which the chlorine is next to the carbonyl group, whilst unsymmetrical ketones give two halogen derivatives, the secondary one predominating.

On boiling the semicarbazones of chloro-ketones with water, hydrogen chloride is eliminated and a ketol formed; thus the semicarbazone of β-chloropropane-γ-one gives β-hydroxypropane-γ-one.

Chlorocarbamide and methyl hexyl ketone give a *chloro-octanone*, m. p. −25°, b. p. 104—108°/20 mm., D 1·0034; the *semicarbazone* has m. p. 133°. Acetophenone forms only ω-chloroacetophenone; cyclic ketones also undergo chlorination. W. O. W.

Action of Dilute Nitric Acid on Starch and on Dextrin. WILLIAM OECHSNER DE CONINCK and ALBERT RAYNAUD (*Rev. gen. Chim. pure appl.*, 1910, **14**, 169—170).—An investigation on the action of dilute nitric acid on dextrin and starch. The dilution of the nitric acid varied from 1 to 5 c.c. of acid (36°Bé) in 50 c.c. water, and the results indicated that the amounts of dextrose formed during the same interval of time increased with the concentration of the acid, but that this increase was less rapid with dextrin than with starch.

With low concentrations, more dextrin than starch underwent hydrolysis, but at the highest concentration dextrin yielded 87·7% dextrose as compared with 90% from starch, indicating that in the former oxidation had to some extent interfered with saccharification.

F. M. G. M.

Modifications Undergone by Nitrated Celluloses and Powders Derived from them, under the Influence of Heat. R. FRIC (*Compt. rend.*, 1912, **154**, 31—32).—The changes produced in nitrated celluloses by heat can be followed by measuring the viscosity of an acetone solution in the usual way. The effect of heating the solid at 110° is to diminish the viscosity of the solution.

W. O. W.

The "Cause" of the Beckmann Rearrangement. PIETER J. MONTAGNE (*Chem. Weekblad*, 1911, **8**, 968—976. Compare Abstr., 1910, i, 623).—In the author's opinion, the Beckmann rearrangement

is a simple exchange of position between the alkyl group attached to carbon and that attached to nitrogen. The assumption of the intermediate formation of an oxime-ester is at variance with the experimental facts. A. J. W.

New Compounds of the Choline Type. G. A. MENGE (*J. Biol. Chem.*, 1911, 10, 399—406).—The *chloride* of *a-methylcholine*, $NClMe_3\cdot CHMe\cdot CH_2\cdot OH$, has been prepared as follows: allyl chloride was converted into the chlorohydrin, and then into the corresponding acetate; this by treatment with hydrochloric acid was converted into the acetate-chloride, and saponified to give the desired chlorohydrin, $CHMeCl\cdot CH_2\cdot OH$. On heating at 100° in a sealed tube with trimethylamine dissolved in alcohol, the choline was obtained as a viscous, yellow oil, from which a hygroscopic, colourless solid separated on cooling. The yellow *platinichloride* decomposes at 254—255°; the *aurichloride* is definitely crystalline: it sinters above 180°, m. p. 198—199·5°.

By condensing monochloroacetone with magnesium alkyl halides, the chlorohydrins of β-methylpropylene αβ-glycol and β-methylbutylene αβ-glycol are obtained. With trimethylamine these yield β-disubstituted cholines.

β-Dimethylcholine chloride, $NClMe_3\cdot CH_2\cdot CMe_2\cdot OH$, is obtained as a colourless, hygroscopic solid. The *platinichloride* crystallises in yellow, short, individual prisms or foliated clusters, which blacken at 240°, decomp. 245°. *β-Methyl-β-ethylcholine chloride*,

$$NClMe_3\cdot CH_2\cdot CMeEt\cdot OH,$$

forms a *platinichloride*, which sinters at 240°, m. p. 242—243° (decomp.). E. F. A.

Stereoisomeric Cobalt Compounds. ALFRED WERNER (*Annalen*, 1911, 386, 1—272).—The author's investigations on the stereoisomeric cobalt compounds have now reached such a stage, that stringent proofs have been obtained for the stereochemical conceptions, and methods which are free from objections have been devised for the determination of the configurations of the various isomerides. A summary of the methods used, and of the results obtained, is given in the present paper, the greater part of the work consisting of hitherto unpublished investigations.

The general results arrived at may be briefly summarised as follows: The investigation of inorganic compounds containing the complex radicle CoA_6 has shown that in all these compounds the six groups *A* are in direct connexion with the central cobalt atom. Any space formula used to represent these compounds must be such that positions occupied by the groups *A* are all equivalent; this follows from the fact that no stereoisomerides are known having the formula $\left[Co\,\frac{A_5}{B}\right]$. It has hitherto been impossible to prepare more than two stereoisomerides of the formula $\left[Co\,\frac{A_4}{B_2}\right]$, so that the groups

A and *B* must occupy the corners of an octahedron, the cobalt atom being in the centre; the plane formula and prism formula would each give three possible isomerides. The groups *B* in the stereoisomerides $\left[Co\,{}^{A_4}_{B_2}\right]$ must consequently occupy the *cis*- and *trans*-positions. Investigation has shown that in all cases when the two groups *B* are replaced by a bivalent group, giving three-, four-, five-, or six-membered rings, the same compound results, no matter whether the *cis*- or *trans*-isomeride was used in the preparation. It appears, therefore, that there is only one position in the complex (the *cis*-position) favourable to the formation of such rings, this being in accordance with the octahedral arrangement of the groups, and in analogy with the formation and non-formation of anhydrides from organic *cis*- and *trans*-isomerides. Use has been made of this result in the determination of the configuration of the various stereoisomerides, but great caution is necessary in drawing conclusions, owing to the ready transformation of one isomeride into the other

Diaquo-salts, $\left[{}^{H_2O}_{H_2O}\,Co\,en_2\right]X_3$.—The *cis*-isomerides have been characterised by their preparation from the carbonato-salts, as also from the hexol- and diol-dicobaltic salts. The *cis*-compounds only are known in the tetrammine series, whereas both *cis*- and *trans*-compounds of the ethylenediamine series have been prepared. The configuration of the *hydroxo-aquo*-salts, $\left[{}^{HO}_{H_2O}\,Co\,en_2\right]X$, is deduced from that of the diaquo-salts because of their formation from the latter by loss of a molecule of acid. Both *cis*- and *trans*-isomerides are known.

Dihalogeno-salts, $[X_2\,Co\,en_2]X_2$.—The two stereoisomeric dichloro-salts are known, both in the tetrammine and diethylenediammine series. The *cis*-isomeride (violeo-salt) is the first product of the action of concentrated hydrochloric acid on the carbonato-salt; it readily changes into the *trans*-isomeride (praseo-salt) under the influence of concentrated hydrochloric acid. The *cis*-dibromotetrammine salts are not known. Stereoisomeric *halogeno-aquo*-salts, $\left[{}^{X}_{H_2O}\,Co\,en_2\right]X_2$, are not known; in all cases the *cis*-isomeride is alone formed.

Halogeno-iso*thiocyanato*-salts, $\left[{}^{H}_{SCN}\,Co\,en_2\right]X$. — Stereoisomeric chloro- and bromo-*iso*thiocyanato-salts are known. Their configuration has to be decided chiefly by their colour (see later), since they so readily undergo transformation. The *iso*thiocyanate group deepens the colour of the cobaltammines, and it follows that the violet chloro-salts and indigo-blue bromo-salts are the *trans*-isomerides, the *cis*-isomerides being red and bluish-red respectively. Similar results hold for the iso*thiocyanato-aquo*-salts, $\left[{}^{SCN}_{H_2O}\,Co\,en_2\right]X_2$, the violet salts forming the *trans*-, and the orange the *cis*-isomerides. The configuration of the *halogeno-amminediethylenediamine* salts, $\left[{}^{X}_{H_3N}\,Co\,en_2\right]X_2$, has been determined by oxidation of the corresponding halogeno-*iso*thio-

cyanato-salts with hydrogen peroxide; both the chloro- and bromo-salts have been prepared. The constitution of the *aquo-ammine-diethylenediamine* salts, $\left[\begin{matrix}H_2O\\H_3N\end{matrix} Co\ en_2\right]X_3$, is determined by their transformation into the halogeno-ammine-salts by interaction with the halogen acids. The stereoisomeric *diisothiocyanato*-salts, $\left[\begin{matrix}SCN\\SCN\end{matrix} Co\ en_2\right]X$, have already been described (Abstr., 1900, i, 86), but the wrong configuration given to them. The *cis*-isomerides are those which were formerly characterised as dithiocyanato-salts, as may be deduced by their oxidation with hydrogen peroxide and subsequent evaporation with hydrochloric acid, whereby the *cis*-chloro-ammine salts are formed. The *trans*-isomerides on oxidation with chlorine yield *trans*-diamminediethylenediaminecobaltic salts, and were formerly characterised as di*iso*thiocyanato-salts. The configuration of the *diamminediethylenediamine* salts, $\left[\begin{matrix}H_3N\\H_3N\end{matrix} Co\ en_2\right]X_3$, was determined by their solubilities, the *cis*- being more readily soluble than the *trans*-isomerides (compare below). The configuration previously ascribed to them (Abstr., 1907, i, 290) is incorrect. Oxidation of the iso*thiocyanatoamminediethylenediamine* salts, $\left[\begin{matrix}SCN\\H_3N\end{matrix} Co\ en_2\right]X_2$, with hydrogen peroxide gives rise to the diammine salts, whereby the structure of the former salts is ascertained. The configuration of the *nitroamminediethylenediamine* salts, $\left[\begin{matrix}O_2N\\H_3N\end{matrix} Co\ en_2\right]X_2$, follows from their formation from the isomeric aquo-ammine salts, or from their transformation into the chloro-ammine salts. On oxidation of the iso*thiocyanatonitrodiethylenediamine* salts, $\left[\begin{matrix}SCN\\O_2N\end{matrix} Co\ en_2\right]X$, with hydrogen peroxide, nitroammine-salts are formed, whereby the configuration of the former salts can be ascertained. Of the *dinitro-diethylenediamine* salts, $[(NO_2)_2\ Co\ en_2]X$, the croceo-salts are the *trans*-, whilst the flavo-salts are the *cis*-isomerides. This is ascertained by their formation from the stereoisomeric diaquo-salts by the action of nitrous acid, the dinitrito-salts first formed transforming into the dinitro-salts. The configuration of the *chloronitro*-salts, $\left[\begin{matrix}Cl\\O_2N\end{matrix} Co\ en_2\right]X$, is ascertained by their transformation into the dinitro-salts by interaction with sodium nitrite.

Influence of the Constitution of the Complex Radicle, $\left[Co \begin{matrix}A_4\\B_2\end{matrix}\right]$, *on the Existence of Stereoisomeric Cobalt Ammonias.*—The *cis*-compounds of the ammonia series are less readily produced than those of the diethylene-diamine series, and transform much more readily into the *trans*-isomerides. *cis*-Dichloro-compounds of the trimethylenediamine series cannot be prepared, all methods of preparation giving the green *trans*-isomerides. The nature of the halogen has an effect, in that, although *cis*- and *trans*-isomerides have been prepared in the dichloro- and dibromo-diethylenediamine series, no *cis*-dibromo-compounds have been obtained in the ammonia series; in neither series could iodo-

compounds be obtained. The influence of the bivalent group Z in the salts [Z Co en_2]X, is shown by the fact that, although sulphito-, carbonato-, oxalato-, and malonato-salts have been prepared, no compounds derived from succinic, malic, and tartaric acids have been obtained. The formation of a seven-ring does not, therefore, take place, which is in accordance with the results obtained with the alkyldiamines (compare Abstr., 1907, ii, 161).

Ionisation Isomerides.—A full list of such compounds is given; for example, the *cis*- and *trans*-isomerides of the chloronitrothiocyanate, nitro*iso*thiocyanato-chloride, and chloro*iso*thiocyanato-nitrite in the diethylenediamine series.

Relation between the Solubility of the Cobalt Ammonias and their Constitution and Configuration.—The *cis*-isomerides are generally more soluble than the *trans*-isomerides. There are exceptions, as, for example, with the dinitrodiethylenediaminecobaltic iodides. It is probable, also, that the solubility of the salt increases with the number of ionogenic radicles.

Relation between the Colour of the Cobalt Ammonias and their Constitution and Configuration.—The chief influence on the colour is exerted by the radicles directly connected with the cobalt atom, and is the only one considered here. No colourless cobalt compounds are known. The inflnence of the element directly attached to the cobalt atom is shown by the series, C, N, S, O, Cl, Br, I, the elements being arranged in the order of their bathochromic action. This series can be extended as follows, when the various radicles are taken into account: CN, CO; NO_2, en, NH_3, NCS; SO_3; OH_2, O·NO, O·Acyl, OH; Cl, Br, I; thus the least-coloured compounds of cobalt are the pale yellow cyanocobaltammonias, $[Co(CN)_6]R_3$. Amines, for example, ethylenediamine, propylenediamine, hydroxylamine, and pyridine, have the same effect as ammonia. It is noteworthy that substitution in the *trans*-position has a much greater bathochromic effect than substitution in the *cis*-position.

Differences in the Reactions of Stereoisomeric Cobalt Ammonias.—Radicles which are in the *cis*-position with respect to each other are not so firmly combined as those in the *trans*-position, and enter into reaction much more readily; for example, by the action of hydrochloric acid on *cis*-dinitrotetramminecobaltic salts, both nitro-groups are replaced by chlorine, with the formation of the *trans*-dichloro-salts, whereas when the *trans*-dinitro-salts are heated with hydrochloric acid, only one nitro-group is replaced, the *trans*-chloronitro-salts being formed. Differences of this kind have caused many difficulties in the determinations of the configuration of the stereoisomerides. These difficulties are especially marked in the case of the *iso*thiocyanato-salts, a full discussion of which compounds is given. Differences also occur in additive reactions; for example, the *trans*-chloroamminediethylenediamine salts readily give the diammine salts when dissolved in liquid ammonia: $\left[\begin{matrix}(1)\quad Cl \\ (6)H_3N\end{matrix}\ Co\ en_2\right]Cl_2 + NH_3 = \left[\begin{matrix}H_3N \\ H_3N\end{matrix}\ Co\ en_2\right]Cl_3$, whereas the *cis*-compounds are unacted on, even after keeping for hours dissolved in liquid ammonia.

Intramolecular Reactions with the Cobalt Ammonias.—The various

cases are summarised in which there occurs: (*a*) Intramolecular reactions with expulsion of ammonia or water; for example, the chlorides, bromides, and sulphates of chloro-aquo- and bromo-aquo-diethylenediaminecobaltic salts are stable, whilst the nitrites, on keeping, change in accordance with the equation: $\left[\begin{smallmatrix}Cl\\H_2O\end{smallmatrix}Co\,en_2\right](NO_2)_2 \longrightarrow \left[\begin{smallmatrix}Cl\\O_2N\end{smallmatrix}Co\,en_2\right]NO_2 + H_2O$. (*b*) Intramolecular reactions in which interchange of the acid-residues takes place; for example, when a drop of water is added to the pure, green *trans*-dichlorodiethylenediamine-cobaltic nitrite, $[Cl_2\ Co\ en_2]NO_2$, it immediately changes into the yellowish-red chloronitrodiethylenediamine chloride, $\left[\begin{smallmatrix}Cl\\O_2N\end{smallmatrix}Co\,en_2\right]Cl$. (*c*) Transformation of stereoisomerides into each other. Direct transformations have hitherto been observed in comparatively few cases, and even then it is probable that intermediate products are formed which have not so far been isolated.

Additive Compounds of the Cobalt Ammonias.—A full discussion is given of cases such as the following: By the addition of silver nitrate to a solution of the intensely-red coloured salt,

$$\left[\begin{matrix}(1)\ SCN\\(2)\ H_3N\end{matrix}Co\,en_2\right]S_2O_6,$$

golden-yellow prisms of the composition $\left[\begin{smallmatrix}SCN\\H_3N\end{smallmatrix}Co\,en_2\right]S_2O_6,AgNO_3$ are obtained. The change in colour observed, and the various reactions of this compound, point to its having the constitution

$$\left[\begin{matrix}AgSCN\\H_3N\end{matrix}Co\,en_2\right]\begin{matrix}NO_3\\S_2O_6\end{matrix},$$

that is, it is a silver thiocyanatoamminediethylenediaminecobaltic salt. The study of such compounds is of great service in elucidating the mechanism of the various reactions of the cobalt ammonias.

Spatial Change of Position during Reactions of the Stereoisomeric Cobalt Ammonias.—(Compare Abstr., 1911, i, 424.)

[With Jos. RAPIPORT.]—*Carbonatodiethylenediaminecobaltic* salts, YX, where $Y = [CO_3\,Co\,en_2]$, are prepared from any dichloro- or dibromo-salt by the action of sodium or potassium carbonate. The mixture with water is boiled until the solution becomes an intense blue colour, when the reaction is complete. The *chloride*, YCl,H_2O, is thus obtained from 1 : 6-dichlorodiethylenediaminecobaltic chloride by interaction with sodium carbonate. The hot filtrate from undissolved salt deposits, on cooling, dark red, flat, columnar crystals, which become anhydrous at 70—80°. It may also be obtained from a concentrated solution of the bromide by shaking with silver chloride. The *bromide*, YBr,H_2O, is obtained from the chloride by precipitation with potassium bromide. On recrystallisation, it deposits partly as hydrated and partly as anhydrous salt. The hydrated salt forms large, dark red, hexagonal, efflorescent columns, the anhydrous salt being brownish-red in colour. One gram of the salt dissolves in 30 c.c. of water at 50°. The *iodide*, YI, is obtained similarly to the bromide, and forms shining, dark red, flat prisms, which are soluble in water to the extent of 1 gram in 70 c.c. of water at 80°. The *nitrate*, YNO_3,H_2O,

results from the interaction of the bromide and silver nitrate; it crystallises in dark bluish-red, shining, flat needles. Twenty c.c. of water dissolve 1 gram at 60°. The *thiocyanate*, YSCN, the *dithionate*, $Y_2S_2O_6,2H_2O$, and the *sulphate*, $Y_2SO_4,5H_2O$, were also obtained by reactions involving double decomposition. They crystallise respectively in red, hexagonal prisms or needles, long, dark red prisms, and reddish-black, flat prisms. The sulphate loses $5H_2O$ at 100°.

[With R. HARTMUTH.]—Oxalatodiethylenediaminecobaltic salts, $[C_2O_4\,Co\,en_2]X$, have been known for some time (compare Abstr., 1899, ii, 660), and an attempt has now been made to introduce ammonia into the radicle to find out if a spatial transformation takes place. As a matter of fact, ammonia does enter into the inner sphere, but cis-*diamminediethylenediaminecobaltic* salts, $Y_2(C_2O_4)X_4$, are alone formed, where $Y = \left[Co\,\begin{matrix}(NH_3)_2\\ en_2\end{matrix}\right]$. Four grams of the oxalatodiethylenediamine salt are heated with 15 c.c. of saturated ammonia solution for two hours in a bomb-tube at 110°; the contents of the tube are taken up with water, the solution concentrated, and potassium iodide added. The sparingly soluble oxalatodiethylenediaminecobaltic iodide is first precipitated, and from the mother liquor brown, monoclinic, columnar crystals of the *iodide oxalate*, $Y_2(C_2O_4)I_4$, are obtained. By interaction with silver chloride, irregular, light yellow, crystalline aggregates of the *chloride oxalate*, $Y_2(C_2O_4)Cl_4$, are obtained. In contradistinction to the aqueous ammonia, liquid ammonia has no action on the oxalato-chloride.

Malonatodiethylenediaminecobaltic salts, YX, where

$$Y = [C_3H_2O_4\,Co\,en_2].$$

—The *hydrogen malonate*, $YC_3H_3O_4$, is obtained from carbonatodiethylenediaminecobaltic bromide by first preparing the hydroxide by shaking the solution with freshly precipitated silver oxide. Malonic acid (2 mols.) is added to the filtrate from the silver bromide, and on concentrating, carmine-red crystals of the desired salt are obtained. By double decomposition with potassium nitrate and ammonium thiocyanate respectively, red, shining leaflets of the *nitrate*, YNO_3, and *thiocyanate*, YSCN, are obtained. Attempts to prepare corresponding salts by using succinic, malic, or tartaric acids were unsuccessful.

[With MARIE POKROWSKA.]—*Sulphitodiethylenediaminecobaltic* salts, YX, where $Y = [SO_3\,Co\,en_2]$.—The *chloride*, $YCl,\frac{1}{2}H_2O$, is obtained by boiling down a solution of sodium sulphite (10 grams) with *trans*-dichlorodiethylenediaminecobaltic chloride (10 grams, free from hydrochloric acid) in 50 c.c. of water to half its bulk. After filtering, dark brown crystals of indefinite shape are deposited. The same results are obtained if the *cis*-dichloro-chloride is used in the preparation. The sulphito-group is co-ordinately connected with the cobalt in the *cis*-position, since on heating with concentrated hydrochloric acid, *cis*-dichlorodiethylenediaminecobaltic chloride is produced. Moreover, the brown colour of the salt shows that the SO_3-radicle is linked up with the cobalt by means of a sulphur valency, thus:

$$\left[\begin{matrix}O\\ |\\ O_2S\end{matrix}\!>\!Co\,en_2\right],$$

since if it were linked through two oxygen atoms it would be red in colour. On triturating the semihydrate with hydrochloric acid, a reddish-brown solution is formed, from which orange-brown, shining scales of the *trihydrate*, $YCl,3H_2O$, can be obtained. The solution gives characteristic precipitates with potassium iodide, acetic acid, and sodium nitrite, and with chloroplatinic acid. On trituration with fuming hydrobromic acid and subsequent gentle warming, green crystals of *trans*-dibromodiethylenediaminecobaltic bromide are obtained. Both hydrates can be dehydrated at 105°. By double decomposition with potassium thiocyanate, brownish-yellow, shining needles or scales of the *thiocyanate*, $YSCN,2H_2O$, are obtained. The *platinichloride*, $Y_2PtCl_6,4H_2O$, forms brown, star-shaped crystals; the *aurichloride*, $YAuCl_4,3H_2O$, crystallises in thin, yellowish-brown, shining scales.

[With K. R. LANGE.]—*Diaquodiethylenediaminecobaltic* salts, YX_3, where $Y = \left[\begin{matrix} H_2O \\ H_2O \end{matrix} Co\ en_2\right]$.—The salts of the *cis*-series are all much more soluble than the *trans*-isomerides. The latter are remarkable in that by precipitation of their aqueous solutions with potassium iodide, the *trans*-hydroxoaquo-iodide is formed and not the diaquo-iodide, which shows that in aqueous solutions the diaquo-salts are hydrolysed in accordance with the equation:

$$[(H_2O)_2\ Co\ en_2]X_3 \rightleftharpoons \left[\begin{matrix} HO \\ H_2O \end{matrix} Co\ en_2\right]X_2 + HX.$$

A number of salts have been prepared in addition to those previously described (compare Abstr., 1907, i, 188). The cis-*nitrate*, $Y(NO_3)_3,H_2O$, was obtained from *cis*-diaquodiethylenediaminecobaltic bromide by the action of concentrated nitric acid at a low temperature. It forms red, glistening plates, and can be dehydrated over calcium chloride. The cis-*sulphate*, $Y_2(SO_4)_3$, was prepared from the bromide by interaction with silver sulphate, and crystallises in red, glistening needles. Other *cis*-salts could not be obtained.

New methods of preparation of the *cis*-bromide are as follows: (1) 10 grams of carbonatodiethylenediaminecobaltic bromide are mixed with 18 c.c. of cold water, and 5 c.c. of concentrated nitric acid added drop by drop. The solution is neutralised with potassium hydroxide, half as much again of the hydroxide added, and then precipitated with sodium bromide (23 grams). (2) The hydroxo-aquobromide is triturated with a little concentrated hydrobromic acid, and then washed with alcohol and ether. The dry product is dissolved in cold water containing a little hydrobromic acid, saturated (at 0°) hydrobromic acid added, and the solution allowed to crystallise in a freezing mixture.

The trans-*nitrate*, $Y(NO_3)_3$, was prepared from the *trans*-bromide by a method similar to that used for the *cis*-salt. It could also be obtained by interaction with silver nitrate. It forms brownish-red needles. The trans-*sulphate*, $Y_2(SO_4)_3$, was obtained from the bromide by interaction with sulphuric acid as brownish-red leaflets. The trans-*dithionate*, $Y_2(S_2O_6)_3$, and the trans-*thiocyanate*, $Y(SCN)_3,\frac{1}{2}H_2O$, crystallise respectively as slender, brownish-red needles and as dark brown plates. The iodide could not be obtained, for the reason already given.

An account is given of the transformation of the diaquodiethylenediaminecobaltic halogenides into dihalogenodiethylenediaminecobaltic salts on keeping for some time or on heating at 105—115°.

A number of *hydroxoaquodiethylenediaminecobaltic* salts, YX_2, where $Y=\left[\begin{smallmatrix}HO\\H_2O\end{smallmatrix}\,Co\,en_2\right]$, have been previously described (Abstr., 1907, i, 189). They have been further studied because the different stereoisomerides may be obtained from the same starting material under conditions of reaction which are only slightly different from each other; thus, in the former paper the *cis*-bromide was prepared from *cis*-dichloro-chloride (violeo-chloride), but it is now shown that when the latter compound is dissolved in concentrated aqueous ammonia and the solution triturated with solid sodium bromide, the *trans*-bromide, YBr_2, is formed. The trans-*thiocyanate* is reddish-brown in colour.

When dichlorovioleo-chloride (5 grams) is dissolved in concentrated ammonia (25 c.c.) by heating on a water-bath, the solution then kept in a vacuum over phosphoric oxide until the odour of ammonia has disappeared, and then precipitated with sodium bromide, a bluish-red precipitate of cis-*chloroamminediethylenediaminecobaltic bromide*,

$$\left[\begin{smallmatrix}Cl\\H_3N\end{smallmatrix}\,Co\,en_2\right]Br_2,$$

is formed. The production of this compound is not due to the intermediate formation of the diaquo-bromide, since this salt when dissolved in concentrated ammonia gives rise to the hydroxoaquo-bromide only.

The *trans*-bromide may also be prepared by carefully heating the *trans*-nitrate with dilute ammonia (1 : 1) until crystals begin to form on the side of the dish.

[With R. Bosshard.]—The formation of carbonatodiethylenediaminecobaltic salts from the stereoisomeric hydroxoaquo-salts has been studied. In all cases one and the same series of carbonato-salts was formed, it being impossible to prepare stereoisomerides. The carbonato-salts were prepared by the action of carbon dioxide either on alkaline solutions or on aqueous solutions of the hydroxoaquo-salts.

Dichlorotetramminecobaltic salts, YX, where $Y=[Cl_2\,Co(NH_3)_4]$.—The constitution of the silver and bismuth salts described previously (Abstr., 1897, ii, 264) must be altered to $\left[\begin{smallmatrix}AgCl\\Cl\end{smallmatrix}\,Co(NH_3)_4\right]Cl_2$ and $\left[\begin{smallmatrix}\frac{Bi}{3}Cl\\Cl\end{smallmatrix}\,Co(NH_3)_4\right]Cl_2$. A new method of preparation of the *cis*-chloride is given. Carbonatotetramminecobalt chloride is shaken up with a saturated (at 0°) solution of hydrogen chloride in absolute alcohol until the evolution of carbon dioxide ceases. The greyish-blue reaction product, which is a mixture of the *cis*- and *trans*-dichloro-salts, after being washed free from acid with alcohol and dried, is extracted with a small quantity of ice-cold water, the *cis*-isomeride going into solution. The filtrate is immediately precipitated with sodium dithionate in order to obtain the violeo-dithionate, from which the chloride and other salts can be obtained in the manner previously described (Abstr., 1908, ii, 42). There is always a considerable loss of violeo-

salt, owing to its ready transformation, in aqueous solution, into chloroaquo-salt. The preparation by means of aqueous hydrochloric acid cooled with liquid air was by no means so satisfactory.

Dichlorodiethylenediaminecobaltic salts, YX, where $Y = [Cl_2 Co en_2]X$. —A new method of preparation of the normal *trans*-chloride is to precipitate an aqueous solution of the acid chloride with solid lithium chloride. The trans-*nitrite*, YNO_2, is obtained as small, green crystals by precipitation of an aqueous solution of the chloride, acidified with acetic acid, with sodium nitrite. When sulphuric acid is used as the precipitant, green crystals of the trans-*hydrogen sulphate*, $YHSO_4$, are obtained. The addition of silver nitrate to a solution of the chloride cooled with a freezing mixture gives a precipitate consisting of greenish-white, glistening leaflets, having the composition $\left[\begin{matrix}AgCl \\ Cl\end{matrix} Co\,en_2\right]_2 \begin{matrix}SO_4 \\ (NO_3)_2\end{matrix}, H_2O$.

New methods of preparation of *cis*-dichlorodiethylenediaminecobaltic salts from carbonatodiethylenediaminecobalt chloride are given; they are similar to those already described for the corresponding tetrammine salts, except that the product of reaction is washed with cold water to free it from impurities, than which the *cis*-dichloro-salt is less soluble. A characteristic cis-*sulphate*, $Y_2SO_4,2H_2O$, is described; it crystallises in small, reddish-violet needles.

[With L. GERB, S. LORIE, and JOS. RAPIPORT.]—*Dibromodiethylenediaminecobaltic* salts, YBr, where $Y = [Br_2 Co en_2.]$—Only the *trans*-isomerides have hitherto been prepared (by Jörgensen), for which new methods of preparation are now given, as follows: (*a*) a solution of cobalt bromide in 10% ethylenediamine is oxidised by leading air through it, and then evaporated to dryness. The residue is then repeatedly treated with hydrobromic acid and evaporated until a uniform green salt remains, which consists of the acid bromide. On treatment with a little water, the *trans*-bromide is obtained. (*b*) Carbonatodiethylenediaminecobalt bromide is heated on the water-bath with a solution of hydrobromic acid (D = 1·49) until the solution is green. On cooling, the acid bromide separates, from which the normal bromide is best obtained by heating at 110° until it no longer gives an acid solution. The trans-*thiocyanate*, YSCN, is precipitated as a canary-green, crystalline salt by the addition of potassium thiocyanate to a solution of the *trans*-bromide.

The methods for the preparation of the cis-*bromide*, YBr, are as follows: (1) a solution of the *trans*-bromide is evaporated on the water-bath several times to a syrupy consistency. On keeping in a vacuum desiccator, black crystals are then obtained, which give a greyish-violet powder; they consist chiefly of the *cis*-isomeride mixed with a little of the *trans*-isomeride. The latter can be extracted with a small quantity of water, leaving the *cis*-form, which can be purified by solution in water and precipitation with sodium bromide. (2) By fission of tetraethylenediaminedioldicobaltic bromide with concentrated hydrobromic acid into diaquo-bromide and the required dibromo-bromide. The diaquo-salt is removed from the mixture by solution in absolute alcohol. (3) From carbonatodiethylenediaminecobaltic bromide by treatment with an alcoholic or aqueous solution of hydrogen bromide

by a method similar to that described for the corresponding dichloro-salts. The cis-*bromide*, YBr, forms scaly crystals, possessing a colour and glance similar to that of graphite. By double decomposition with the appropriate salts of the alkali metals, the following compounds were prepared. The cis-*iodide*, YI, is similar in appearance to the bromide; the cis-*nitrate*, YNO_3, forms small, greyish-violet crystals, as also does the cis-*thiocyanate*, $YSCN,H_2O$; the crystals of the cis-*dithionate*, $Y_2S_2O_6$, are somewhat lighter in colour than those of the other salts.

Chlorobromodiethylenediaminecobaltic salts, YX, where

$$Y = \left[\begin{matrix}Cl\\Br\end{matrix} Co\ en_2\right]X.$$

—Both the *cis*- and *trans*-isomerides have been prepared; the former are readily obtained pure, the latter only with difficulty, since they are generally mixed with *trans*-dibromo-salts. Two methods of preparation are given: (1) Two grams of chloroaquodiethylenediamine-cobaltic bromide are covered with 2 c.c. of concentrated hydrobromic acid, and the mixture heated until complete solution takes place. On cooling, a mixture of the green and violet salt is obtained, which is washed with alcohol and ether, dried, and then treated with a small quantity of water to dissolve out the green salt. The violet salt (*cis*-isomeride) is collected, washed with water and alcohol, and dried. The green filtrate gives precipitates with metallic salts, which give analytical results corresponding with a mixture of dibromo- and chlorobromo-salts. (2) Chloroaquodiethylenediaminecobaltic bromide is heated for two hours at 110°, whereby a mixture of the *cis*- and *trans*-chlorobromo-bromides is produced. This is separated as in (1), the *trans*-nitrate being precipitated from the green filtrate by ammonium nitrate.

The trans-*nitrate*, YNO_3, forms small, light green, glistening leaflets. The trans-dithionate, $Y_2S_2O_6$, and trans-*thiocyanate*, YSCN, are prepared from the green filtrate mentioned above by double decomposition with the appropriate alkali salts; they form respectively glistening, green, flat crystals, and a light green precipitate. The cis-*bromide*, YBr,H_2O, is a greyish-violet, microcrystalline salt; the cis-*nitrate*, YNO_3, forms dark violet needles, and the cis-*dithionate*, $Y_2S_2O_6$, small, violet leaflets.

When the *cis*-bromide is gently warmed with concentrated hydrobromic acid until a solution is formed, it is changed into *trans*-dibromodiethylenediaminecobaltic bromide, which is deposited on cooling in canary-green crystals.

Halogenoaquodiethylenediaminecobaltic salts, $\left[\begin{matrix}X\\H_2O\end{matrix} Co\ en_2\right]X_2$.—Only the *cis*-isomerides have so far been obtained; the cold aqueous solutions are fairly stable, but, on heating, complicated changes take place. By the action of concentrated aqueous ammonia on the chloroaquo- and bromoaquo-bromides, hydroxochloro- and hydroxobromo-bromides are obtained.

cis-*Chloroaquodiethylenediaminecobaltic* salts, YX_2, where

$$Y = \left[\begin{matrix}Cl\\H_2O\end{matrix} Co\ en_2\right].$$

—The *sulphate*, $YSO_4,1\frac{1}{2}H_2O$, is prepared by heating 20 grams of *trans*-dichlorodiethylenediaminecobaltic chloride with 20 c.c. of water until a deep blue solution is obtained. After cooling, and keeping for one hour, ammonium sulphate (10 grams) is added; on keeping for a further twelve hours, bluish-red crystals of the sulphate are deposited, mixed with some green crystals which can be removed by shaking with a little cold water. The sulphate dissolves in concentrated ammonia, and the solution gives a bluish-red precipitate of chloroamminediethylenediaminecobaltic bromide with concentrated hydrobromic acid. The *chloride*, YCl_2, and the *bromide*, YBr_2,H_2O, are obtained from the sulphate by interaction with the respective halogen acids. The former is microcrystalline, and the latter forms small, crystalline leaflets; both are reddish-violet in colour. The *bromide-nitrate*, $YBrNO_3$, prepared from the bromide and lithium nitrate, is reddish-brown in colour. The *nitrite*, $Y(NO_2)_2$, from the chloride and sodium nitrite gives dark violet micro-crystals. It is unstable, changing to *cis*-chloronitrodiethylenediaminecobaltic nitrite.

[With R. SCHMIDT.]—cis-*Bromoaquodiethylenediaminecobaltic* salts, YX_2, where $Y = \left[\begin{matrix} Br \\ H_2O \end{matrix} Co\, en_2\right]$.—The following methods are given for the preparation of the *bromide*, YBr_2,H_2O. (1) A solution of neutral 1 : 6-dichlorodiethylenediaminecobaltic chloride containing nitric acid is heated with a concentrated solution of silver nitrate until it assumes a Bordeaux-red colour. After collecting the silver bromide, the filtrate is saturated with sodium bromide, first filtering off any more silver bromide which may be formed. After a few hours the bromide has deposited as a violet, microcrystalline powder. (2) A concentrated solution of the *trans*-dibromo-bromide is heated at 40° until it becomes violet in colour; after cooling, it is saturated with sodium bromide. Any green crystals of praseo-bromide which are precipitated with the bromoaquo-bromide are removed by fractional solution in ice-cold water, the praseo-bromide being the lesser soluble salt. (3) A solution of *trans*-dibromonitrate is treated similarly to the dibromo-bromide, except that it is heated over the bare flame. (4) The carbonatochloride or bromide is treated with concentrated hydrobromic acid ($D = 1·4$). The bromoaquo-bromide is separated from the less soluble *cis*-dibromo-bromide, which is formed at the same time, by fractional solution. (5) *cis*-Diaquo-bromide is heated at 40° with just enough water to give complete solution until a violet-coloured solution is obtained; the bromoaquo-salt is then precipitated with sodium bromide.

The bromide forms dark violet, leaf-like crystals. By double decomposition with sodium nitrate and sodium nitrite respectively, it gives the *nitrate*, $Y(NO_3)_2,H_2O$, and *nitrite*, $Y(NO_2)_2$, as bluish-violet, crystalline powders. When triturated with Erdmann's salt,

$$[(NO_2)_4Co(NH_3)_2]NH_4,$$

it gives a yellowish-green, tetranitrodiamminecobalt compound.

Hydroxohalogeno-salts, $\left[\begin{matrix} HO \\ X \end{matrix} Co\ A_4\right]X$.—*Hydroxochlorotetrammine-cobaltic dithionate*, $\left[\begin{matrix} HO \\ Cl \end{matrix} Co\,(NH_3)_4\right]_2 S_2O_6$, is precipitated as a violet-blue

salt when solid chloroaquotetramminecobaltic chloride is dissolved in a saturated solution of sodium dithionate in concentrated ammonia, ammonium dithionate remaining in solution. The colour corresponds with that of the *cis*-dichlorotetrammine salts. The corresponding *hydroxochlorodiethylenediaminecobaltic bromide*, $\left[\begin{smallmatrix}HO\\Cl\end{smallmatrix}Co\,en_2\right]Br$, is obtained as a brownish-violet, crystalline paste when chloroaquodiethylenediaminecobaltic bromide is treated with concentrated ammonia; when heated with concentrated hydrogen chloride, this salt gives a mixture containing a little 1 : 6-dichloro- with much 1 : 2-dichloro-diethylenediaminecobaltic chloride. cis-*Hydroxobromodiethylenediaminecobaltic bromide*, $\left[\begin{smallmatrix}HO\\Br\end{smallmatrix}Co\,en_2\right]Br$, is similarly obtained as a brownish-violet salt from the bromoaquo-bromide and ammonia. When warmed with a little water, addition takes place with the formation of the *cis*-hydroxoaquo-bromide; similarly, when triturated with concentrated hydrobromic acid, the *cis*-diaquo-bromide is obtained.

*Chloro*iso*thiocyanatodiethylenediaminecobaltic* salts, YX, where $Y = \left[\begin{smallmatrix}Cl\\SCN\end{smallmatrix}Co\,en_2\right]$.—A few of the *trans*-isomerides, which were, however, impure, have been described previously (Abstr., 1900, i, 86). The trans-*thiocyanate*, YSCN, is obtained by precipitating a solution of 1 : 6-dichlorodiethylenediaminecobaltic chloride with potassium thiocyanate. The precipitate consists of a mixture of about two-thirds of the *trans*- and one-third of the *cis*-isomeride. By appropriate treatment the pure *trans*-isomeride is obtained as sparingly soluble, violet leaflets. When triturated with hydrobromic acid, it gives glistening, bluish-violet crystals of the trans-*bromide*, $YBr,2H_2O$. This salt may also be prepared from praseo-chloride (Abstr., 1907, i, 291). With sodium dithionate, it gives bluish-violet, glistening crystals of the trans-*dithionate*, $Y_2S_2O_6$, and with perchloric acid, violet leaflets of the trans-*perchlorate*, $YClO_4$. The perchlorate may also be obtained directly from the *trans*-dichlorothiocyanate and perchloric acid.

The *trans*-isomerides dissolve readily in liquid ammonia, giving reddish-yellow solutions which deposit mixtures of the stereoisomeric *iso*thiocyanatoammine salts. If the *trans*-perchlorate is boiled with sodium nitrite in concentrated aqueous solution until a reddish-brown colour is obtained, the solution cooled, and ammonium thiocyanate added, an isomorphous mixture of the 1 : 6-chloro*iso*thiocyanato- and 1 : 6-nitro*iso*thiocyanato-thiocyanates is precipitated. If the solution is boiled until brown in colour, small quantities of the *cis*-nitro*iso*thiocyanato-salt crystallise on cooling. On heating a solution of *trans*-chloro*iso*thiocyanato-bromide with potassium thiocyanate and cooling, needles of the *trans*-di*iso*thiocyanato-thiocyanate separate, and from the mother liquor small quantities of the *cis*-isomeride can be obtained; oxidation of the *trans*-salt with hydrogen peroxide gives the *trans*-diammine salt.

On boiling a concentrated solution of the *trans*-chloro*iso*thiocyanato-bromide (1 mol.) with silver nitrate (3 mols), filtering from silver bromide, and cooling, light violet, slender needles of an *additive com-*

pound, $\left[\begin{matrix}\mathrm{Cl} \\ \mathrm{AgSCN}\end{matrix}\mathrm{Co\ en_2}\right](NO_3)_2$, are obtained. On boiling the aqueous solution of this salt, silver chloride is slowly precipitated.

cis-*Chloroisothiocyanatodiethylenediaminecobaltic chloride*, YCl, is obtained in the purification of the *trans*-thiocyanate in the form of bluish-red needles. It is purified by transformation into the perchlorate and precipitation of the solution of this salt with concentrated hydrochloric acid. By double decomposition of a solution of the perchlorate with the appropriate salts of the alkali metals, the following compounds were obtained: cis-*Dithionate*, $Y_2S_2O_6,H_2O$, brownish-red needles; cis-*nitrate*, YNO_3, dark bluish-red needles; cis-*sulphate*, Y_2SO_4, violet-red powder. The cis-*bromide*, $YBr,1\frac{1}{2}H_2O$, was obtained from the chloride by interaction with hydrobromic acid. A method of preparation of the *cis*-chloride from *cis*-*iso*thiocyanatonitro-chloride by interaction with hydrochloric acid is also given.

The action of hydrogen peroxide, liquid ammonia, potassium thiocyanate, sodium nitrite, and silver nitrate on the *cis*-salts is fully described.

Bromoisothiocyanatodiethylenediaminecobaltic salts, YX, where $Y = \left[\begin{matrix}\mathrm{Br} \\ \mathrm{SCN}\end{matrix}\mathrm{Co\ en_2}\right]$.—Both series of isomerides are known, but the *cis*-salts are difficult to isolate, since in aqueous solution they are readily transformed into aquo-salts. The *trans*-isomerides on oxidation with hydrogen peroxide under certain conditions give 1 : 6-bromoamine salts, and under other conditions 1 : 6-dibromo-salts. Hydrogen peroxide completely oxidises the thiocyanate residue of the *cis*-isomerides, but if the aqueous solution is kept some time before hydrogen peroxide is added, a salt of the aquo-series is formed, which then gives rise to the bromoammine salt. With ammonia both isomerides give a mixture of *cis*- and *trans*-*iso*thiocyanatoammine-diethylenediaminecobaltic salts.

The trans-*thiocyanate*, YSCN, is prepared from 1 : 6-dibromo-diethylenediaminecobaltic bromide by precipitation with potassium thiocyanate. The green precipitate and mother liquor are heated until a deep red solution is obtained. On cooling, and further addition of potassium thiocyanate, green, glistening needles of the required salt are obtained. Trituration with concentrated hydrobromic acid gives dark blue, prismatic crystals of the *trans*-bromide, $YBr,2H_2O$, and precipitation with perchloric acid, the trans-*perchlorate*, $YClO_4$, as dark blue, almost black, slender needles. The trans-*dithionate*, $Y_2S_2O_6$, forms violet-blue leaflets.

Three methods of preparation of the cis-*bromide*, YBr, are fully described, namely, from 1 : 6-dibromodiethylenediaminecobaltic bromide, 1 : 2-aquo*iso*thiocyanatodiethylenediaminecobaltic dithionate, and 1 : 2-nitro*iso*thiocyanatodiethylenediaminecobaltic sulphate. It forms garnet-red, glistening, prismatic crystals, and is used as a source of preparation of the other salts by methods involving double decomposition. The cis-*nitrate*, YNO_3, is violet-brown in colour, the cis-*dithionate*, $Y_2S_2O_6$, brownish-red, whilst the cis-*sulphate*, Y_2SO_4, gives reddish-lilac, silky, thin leaflets.

iso*Thiocyanatoaquodiethylenediaminecobaltic* salts, YX_2, where

$$Y = \left[\begin{matrix} SCN \\ H_2O \end{matrix} \text{ Co en}_2\right].$$

—Both series of isomerides have been obtained, whereas with all other acidoaquo-salts it has been possible to prepare one series only, either the *cis*- or *trans*-. The salts of the *cis*-series are yellowish-red to crimson in colour, whilst those of the *trans*-series are violet; the former are obtained from the stereoisomeric chloro*iso*thiocyanato-salts by the action of concentrated ammonia, and the latter from the same salts by the action of potassium hydroxide.

The cis-*dithionate*, YS_2O_6,H_2O, is prepared by warming 1 : 6-chloro-*iso*thiocyanatodiethylenediaminecobaltic bromide with concentrated ammonia until a red solution is formed. The cooled solution is then poured into absolute alcohol, the precipitate dried on a porous plate, dissolved in cold water, and glacial acetic acid added to the solution until a precipitate begins to form. On further keeping, orange-coloured needles of the dithionate separate. With potassium thiocyanate the solution gives a crimson precipitate of the cis-*thiocyanate*, $Y(SCN)_2$. With hydrogen peroxide, the dithionate gives a mixture of the *cis*- and *trans*-chloroammine salts; with concentrated hydrochloric acid, *cis*-chloro*iso*thiocyanato-salts; with nitrous acid, cis-*nitro*iso*thiocyanato-diethylenediaminecobaltic dithionate*, $\left[\begin{matrix} O_2N \\ SCN \end{matrix} \text{ Co en}_2\right]_2 S_2O_6$, in the form of slender, yellow needles; with potassium thiocyanate, *cis*-di*iso*thiocyanato-salts. With silver nitrate and perchloric acid, an orange-coloured *additive product*, $\left[\begin{matrix} AgSCN \\ H_2O \end{matrix} \text{ Co en}_2\right]\begin{matrix}(ClO_4)_2 \\ NO_3\end{matrix},2H_2O$, is obtained.

The trans-*bromide*, $YBr_2,2H_2O$, is prepared as follows: 1 : 6-chloro-*iso*thiocyanatothiocyanate dissolves in potassium hydroxide to a red solution; on cooling, brownish-red leaflets of 1 : 6-*hydroxo*iso*thio-cyanato-thiocyanate*, $\left[\begin{matrix} HO \\ SCN \end{matrix} \text{Co en}_2\right]SCN,H_2O$, separate. These are dissolved in a little water, excess of concentrated hydrobromic acid added, and the solution kept over sulphuric acid in a desiccator. After a few days, dark red crystals of the required bromide separate. From this salt, by the method of double decomposition, the trans-*thio-cyanate*, $Y(SCN)_2,H_2O$, is obtained as a violet precipitate, the trans-*nitrate*, $Y(NO_3)_2,H_2O$, as bluish-red needles, and the trans-*nitrite*, $Y(NO_2)_2$, as dark violet-red crystals. On the addition of excess of silver nitrate to a well-cooled solution of the nitrate, bright red needles of an *additive product*, $\left[\begin{matrix} H_2O \\ Ag_2SCN \end{matrix} \text{Co en}_2\right](NO_3)_4,H_2O$, are deposited.

On oxidation with nitric acid or hydrogen peroxide, and subsequent evaporation with concentrated hydrochloric acid, the *trans*-aquo*iso*-thiocyanato-salts give only *trans*-chloroammine salts.

When solid sodium nitrite is added to a concentrated solution of 1 : 6-*iso*thiocyanatoaquo-nitrate acidified with a few drops of acetic acid, a bright red precipitate of 1 : 6-*nitrito*iso*thiocyanatodiethylene-diaminecobaltic nitrite*, YNO_2,H_2O, where $Y = \left[\begin{matrix} ONO \\ SCN \end{matrix} \text{ Co en}_2\right]$, is

produced; with potassium thiocyanate the solution gives red needles of the 1 : 6-*thiocyanate*, YSCN.

Chloroamminediethylenediaminecobaltic salts, YX_2, where Y = $\left[\begin{matrix}Cl\\H_3N\end{matrix}Co\ en_2\right]$.—The isomerides of this series are best distinguished by means of the dithionates; the *cis*-dithionate forms thick crystals, whilst the *trans*-dithionate crystallises in long, glistening needles. Both series of salts are bluish-red in colour. The *trans*-salts react very quickly with liquid ammonia, forming diammine salts, whereas the *cis*-isomerides are scarcely acted on. Jörgensen has already prepared a number of the *cis*-isomerides.

The best method of preparation for the *cis*-chloride, YCl_2, is the trituration of 1 : 6-dichlorodiethylenediaminecobaltic chloride with concentrated ammonia. The green salt first dissolves, and then a red paste of the required chloride separates. The addition of solid sodium perchlorate to a solution of the chloride precipitates long, red prisms of the cis-*chloride-perchlorate*, $YCl(ClO_4)$; on recrystallisation from concentrated hydrochloric acid it is transformed into the chloride. The cis-*nitrite*, $Y(NO_2)_2$, forms brick-red crystals. The actions of sodium and silver nitrites, of potassium thiocyanate, and of liquid ammonia on the *cis*-chloride are fully described, as also the changes which aqueous solutions of the *cis*-nitrite undergo on warming.

To prepare the trans-*chloride*, YCl_2,H_2O, 1 : 6-chloro*iso*thiocyanatodiethylenediaminecobaltic thiocyanate is oxidised with hydrogen peroxide in aqueous solution acidified with sulphuric acid. Precipitation with hydrochloric acid then gives a chloride-sulphate, which is recrystallised from hydrochloric acid several times, and the aqueous solution then precipitated with barium chloride to remove the sulphuric acid. It forms bright ruby-red prisms. It may also be prepared from 1 : 6-nitroammine salts by heating with concentrated hydrochloric acid, and from 1 : 6-dichloro-salts by the action of a methyl-alcohol solution of ammonia. The trans-*chloride-perchlorate*, $YCl(ClO_4)$, is prepared from 1 : 6-chloro*iso*thiocyanatodiethylenediaminecobaltic perchlorate by a method similar to that used for the chloride; it forms bright red, glistening leaflets or flat needles. The trans-*chloride hydrogen sulphate*, $YCl(HSO_4)$, is obtained by repeated evaporation on the water-bath of 1 : 6-nitroamminedithionate with hydrochloric acid; it crystallises in thick, ruby-red plates. The trans-*dithionate*, YS_2O_6,H_2O, crystallises as bright red, slender needles when sodium dithionate is added to a solution of the chloride-perchlorate. The *dichromate*, *nitrate*, and *nitrite* have also been obtained. The actions of sodium and silver nitrites, of potassium thiocyanate, and of liquid ammonia on the *trans*-chloride-perchlorate are fully described, as also the changes which aqueous solutions of the *trans*-nitrite undergo on keeping or on warming.

Bromoamminediethylenediaminecobaltic salts, YX_2, where Y = $\left[\begin{matrix}Br\\H_3N\end{matrix}Co\ en_2\right]$.—Both series of isomerides have been prepared, the *cis*-isomerides being the more easily obtained. The determination of their configuration depends on the formation of the *trans*-isomerides from *trans*-bromo*iso*thiocyanato-salts by oxidation with hydrogen

peroxide. Both series are very similar in colour. The *cis*-dithionate forms short, compact crystals, whilst the *trans*-isomeride gives long, slender needles; also, the former salt readily dissolves in concentrated hydrobromic acid, with the formation of the bromide, whereas the latter is unaltered.

[With W. E. Boës.]—The cis-*bromide*, $YBr_2,2H_2O$, is obtained when moist 1 : 6-dibromodiethylenediaminecobaltic bromide is treated at a low temperature with ammonia (1 : 1), drop by drop, until the green colour changes to a dark violet. At higher temperatures, the diammine-salt is produced, owing to the addition of a further molecule of ammonia. When recrystallised from water, it forms bundles of reddish-violet, glistening needles; when precipitated from the aqueous solution by the addition of concentrated hydrobromic acid, the anhydrous salt, YBr_2, is obtained as dark brownish-red prisms or needles. It may also be prepared (1) by the action of ammonium bromide on tetraethylenediaminediaquotetroldicobalticobaltous sulphate, and (2) by the action of hydrobromic acid on 1 : 2-nitroamminediethylenediaminecobaltic salts or on 1 : 2-aquoamminediethylenediaminecobaltic salts. By appropriate double decomposition the following salts were obtained: cis-*bromide-nitrate*, $YBr(NO_3)$, as reddish-violet crystals; the cis-*dithionate*, YS_2O_6, as reddish-violet, thin leaflets; the cis-*platinochloride*, $YPtCl_4$, as reddish-brown leaflets. The cis-*nitrate*, $Y(NO_3)_2$, was obtained from the bromide by trituration with concentrated nitric acid as dark reddish-violet, long, rectangular columns.

The trans-*dithionate*, YS_2O_6, is obtained from 1 : 6-bromo*iso*thiocyanatodiethylenediaminecobaltic bromide by oxidation at 50° with hydrogen peroxide in aqueous solution acidified with acetic acid, and subsequent precipitation with sodium dithionate. It forms bluish, rose-coloured, slender needles. With ammonium iodide the solution gives reddish-brown, glistening, flat needles of the trans-*iodide*, YI_2,H_2O. The trans-*bromide*, YBr_2,H_2O, was prepared from 1 : 6-aquoamminediethylenediaminecobaltic bromide by evaporation with concentrated hydrobromic acid on the water-bath. It forms large, dark reddish-violet prisms, and serves as the source of the trans-*nitrate*, $Y(NO_3)_2,H_2O$, and the trans-*perchlorate*, $Y(ClO_4)_2$, the latter crystallising in violet needles.

Aquoamminediethylenediaminecobaltic salts, YX_3, where

$$Y=\left[\begin{matrix}H_2O\\H_3N\end{matrix}\ Co\ en_2\right].$$

—Both series of isomerides have been prepared. They are obtained by the action of potassium hydroxide or of freshly precipitated silver oxide on the stereoisomeric chloroammine- and bromoammine-diethylenediaminecobaltic salts. In every case, partial transformation takes place, so that a mixture of the isomerides is produced. The product of action of the alkali is an hydroxoammine salt, the aquoammine salt being produced when the solution is acidified. Potassium hydroxide produces a greater relative transformation than silver oxide; more *trans*-isomeride seems to be produced at low than at ordinary temperatures. The mixture of the isomerides is separated by taking advantage of the fact that the *trans*-aquoammine-bromide is much less soluble in dilute

hydrobromic acid than the *cis*-isomeride. The isomerides can be distinguished from each other (1) by transformation into the chloroamminedithionate (*q.v.*) by warming with hydrochloric acid, and subsequent precipitation with sodium dithionate; (2) by warming the aqueous solution to which sodium nitrite and a little acetic acid has been added to 60—70°. A yellow solution is produced, which, on the addition of sodium dithionate, gives an insoluble precipitate if the *cis*-isomeride is present, or a precipitate which can be recrystallised from water if the *trans*-isomeride is present.

The trans-*bromide*, YBr_3,H_2O, forms pale brick-red needles, and is used as the source of other salts, methods of double decomposition being employed. The trans-*iodide*, YI_3,H_2O, forms brownish-red, flat, prismatic crystals; the trans-*nitrate*, $Y(NO_3)_3$, crystallises in fire-red, glistening prisms; the trans-*platinichloride*, $Y_2(PtCl_6)_3,2H_2O$, gives small, dark, brownish-red crystals, and the trans-*platinochloride*, $Y_2(PtCl_4)_3,2H_2O$, forms slender, light brown crystals.

The cis-*bromide*, YBr_3,H_2O, forms clumps of small, red crystals.

The *diisothiocyanatodiethylenediaminecobaltic* salts, YX, where $Y = [(SCN)_2 Co\, en_2]$, have already been described (compare Bräunlich, Abstr., 1900, i, 86). Their true configuration has now been determined as follows. By violent oxidation with concentrated nitric acid and subsequent evaporation with hydrochloric acid, the *trans*-isomerides give mainly *trans*-chloroammine salts, together with some *trans*-diammine salts; oxidation with hydrogen peroxide gives only the latter salts. Under the same treatment the *cis*-isomerides give respectively *trans*-dichloro-salts, together with a little *cis*-chloroammine-salt, and *cis*-chloroammine salt. On oxidation with chlorine the *trans*-isomerides give *trans*-diammine salts, and the *cis*-isomerides, *trans*-dichloro-salts.

[With C. Rix.]—A new method of preparing the *cis*-salts is as follows: 1 : 2-nitroso*iso*thiocyanatodiethylenediaminecobaltic thiocyanate is evaporated with hydrochloric acid, whereby pure *cis*-di*iso*thiocyanatodiethylenediaminecobaltic chloride, $YCl,\frac{1}{2}H_2O$, is obtained.

The solubilities at 25° of the various salts in grams per 50 c.c. of water containing acetic acid are as follows: chloride, 0·2766; bromide, 0·1996; iodide (at 24°), 0·465; nitrate, 0·1968; thiocyanate, 0·1860.

Stereoisomeric *diamminediethylenediaminecobaltic* salts, YX_3, where $Y = [(NH_3)_2 Co\, en_2]$, have already been described (Abstr., 1907, i, 290), but the wrong configuration has been assigned to them; those which were formerly characterised as *cis*-compounds are now found to be the *trans*-isomerides, and vice-versa. The evidence for this is based on their relation with the di*iso*thiocyanato- and *iso*thiocyanato-ammine-salts, which has already been indicated, and on the resolution of the *cis*-compounds into the optically active isomerides. The *trans*-salts are sparingly soluble, whilst the *cis*-salts are readily soluble. A new method of preparation is described, by the oxidation of the *iso*thiocyanatoamminediethylenediaminecobaltic salts with hydrogen peroxide in the presence of halogen acid.

[With R. Samanek.]—Mixtures of the two series of salts have also been obtained by the action of liquid ammonia on the following compounds: 1 : 6-dichloro-, 1 : 6-dibromo-, and 1 : 2-dibromo-diethylene-

diaminecobaltic salts; 1 : 6-chloroammine-, 1 : 6- and 1 : 2-bromoammine-diethylenediaminecobaltic salts. The separation of the isomerides can be brought about by taking advantage of the fact that the bromide of the *trans*-series is only sparingly soluble in hydrobromic acid, whereas the *cis*-bromide is readily soluble; or, better still, by precipitation of concentrated solutions of the salts with sodium dithionate, whereby the *trans*-dithionate is obtained, it being practically insoluble in water; from the mother liquor the *cis*-periodide is precipitated by the addition of a solution of iodine in hydriodic acid, and by trituration of this salt with sodium thiosulphate the *cis*-iodide is obtained.

In all reactions leading to the formation of diammine salts, the *cis*-isomerides are formed in preponderating amount. If the action of ammonia on the 1 : 6-dichloro-salts is not sufficiently energetic, some 1 : 2-chloroammine salt is formed.

iso*Thiocyanatoamminediethylenediaminecobaltic* salts, YX_2, where $Y = \left[\begin{matrix} SCN \\ H_3N \end{matrix} Co\ en_2\right]$.—The two series of isomerides have been obtained, and are very important, because of their genetic relations with other series, in the determination of configurations, etc. A mixture of both isomerides is always obtained in their preparation, no matter whether 1 : 2-chloro-, 1 : 2-bromo-, or 1 : 6-chloro-, 1 : 6-bromo-*iso*thiocyanatodiethylenediaminecobaltic salts are used to obtain them by interaction with liquid ammonia. The relative proportion of the isomerides produced is not independent of the nature of the ionogenic radicle in the salt used.

The cis- and trans-*thiocyanates*, $Y(SCN)_2$, are obtained by dissolving 1 : 6-chloro*iso*thiocyanatodiethylenediaminecobaltic thiocyanate in liquid ammonia and allowing the solution to evaporate at the ordinary temperature. The residue is dissolved in water containing acetic acid, and, on keeping, the *trans*-thiocyanate is deposited as slender, glistening, reddish-orange needles; the *cis*-thiocyanate is precipitated from the mother liquors by the addition of much potassium thiocyanate in the form of reddish-brown, crystalline crusts. By appropriate double decomposition the following salts were obtained: cis-*dithionate*, YS_2O_6, brilliant, orange-red leaflets; cis-*iodide*, YI_2, short, columnar, reddish-brown crystals; trans-*iodide*, YI_2,H_2O, small, brick-red prisms. The trans-*bromide-dithionate*, $Y_2Br_2(S_2O_6),2H_2O$, was prepared by trituration of the thiocyanate with hydrobromic acid and subsequent precipitation with sodium dithionate; it forms brownish-red, prismatic crystals. With silver nitrate the *cis*-dithionate gives glistening, yellow crystals of an *additive product*, $\left[\begin{matrix} H_3N \\ AgSCN \end{matrix} Co\ en_2\right]\begin{matrix} S_2O_6 \\ NO_3 \end{matrix}$, whilst the *trans*-perchlorate, prepared from the thiocyanate and perchloric acid, gives yellow needles of the *additive product*, $\left[\begin{matrix} H_3N \\ Ag_2SCN \end{matrix} Co\ en_2\right](NO_3)_4$.

A detailed account is given of the action of oxidising agents and of potassium thiocyanate on the *cis*- and *trans*-isomerides.

Nitratoamminediethylenediaminecobaltic salts, YX_2, where

$$Y = \left[\begin{matrix} O_3N \\ H_3N \end{matrix} Co\ en_2\right],$$

are obtained by the evaporation of the stereoisomeric aquoammine-diethylenediaminecobaltic nitrates with concentrated nitric acid. In the preparation of the *trans*-isomeride from the 1 : 6-aquoammine salt, some *cis*-isomeride is formed at the same time, but the two are readily separated by taking advantage of the fact that the *cis*-dithionate is almost insoluble in water. Their configuration is determined by evaporation with concentrated hydrochloric acid, which gives the corresponding chloroammine salts. Liquid ammonia gives a mixture of the stereoisomeric diammine salts.

The cis-*nitrate*, $Y(NO_3)_2$, forms small, glistening, orange-red crystals; the cis-*dithionate*, YS_2O_6,H_2O, is an orange-coloured powder. The trans-*dithionate*, YS_2O_6, crystallises in orange-coloured needles.

[With W. E. Boës].—*Nitroamminediethylenediaminecobaltic* salts, YX_2, where $Y = \left[\begin{matrix}O_2N\\H_3N\end{matrix} Co\ en_2\right]$.—Both series of isomerides have been prepared, and are distinguished from each other by the fact that the *cis*-salts are much more soluble than the *trans*-salts, this difference being especially marked in the dithionates. The configuration is best decided by evaporation of the salt to dryness with hydrochloric acid, solution of the residue in water, and precipitation with sodium dithionate of the chloroamminediethylenediaminecobaltic dithionate, the *cis*- and *trans*-isomerides of which are very characteristic.

The cis-*bromide*, YBr_2, is obtained by adding an excess of a saturated solution of sodium nitrite to a saturated (at 25°) solution of 1 : 2-aquoamminediethylenediaminecobaltic bromide, acidifying with acetic acid, and warming at 40° until the solution becomes orange-yellow in colour. After keeping for twenty-four hours a precipitate consisting of a mixture of the bromide and nitrite is deposited; it is dissolved in water, and the solution saturated at 35° with potassium bromide. On cooling, large, dark yellow plates of the bromide are obtained. The following salts were obtained from the bromide, for the most part by the usual methods of double decomposition. The cis-*chloride*, YCl_2, forms orange-yellow prisms or else a microcrystalline precipitate; the cis-*iodide*, YI_2, crystallises in reddish-brown needles; the cis-*nitrate*, $Y(NO_3)_2$, in flat, tabular, or needle-shaped crystals. The cis-*dithionate*, YS_2O_6, forms small, golden-yellow leaflets, whilst the cis-*sulphate*, YSO_4, crystallises in long, radiating, light yellow, prismatic needles. The cis-*bromide-nitrate*, $YBr(NO_3)$, is prepared by the gradual addition of concentrated nitric acid to a well-cooled solution of the nitrate; it forms large, glistening, reddish-brown prisms.

The following methods of preparation of the *cis*-isomerides are also described: (1) By the action of silver nitrite on 1 : 2-chloroammine-diethylenediaminecobaltic chloride. (2) By the action of ammonia on 1 : 6-dinitrodiethylenediaminecobaltic salts. (3) By oxidation of 1 : 2-nitro*iso*thiocyanatodiethylenediaminecobaltic salts.

The trans-*nitrate*, $Y(NO_3)_2,\frac{1}{2}H_2O$, is prepared by dissolving 1 : 6-nitronitratodiethylenediaminecobaltic nitrate in liquid ammonia, and allowing the solution to evaporate spontaneously. The residue is recrystallised from water, whereby a mixture of large, dark brown plates and small, light yellow crystals is obtained, which are

mechanically separated. The latter crystals consist of 1 : 6-dinitro-nitrate, whilst the former are the required *trans*-nitrate, and, after further recrystallisation, are obtained as flat, rhombic tablets. By appropriate double decomposition, the nitrate yielded the following salts: the trans-*iodide*, YI_2,H_2O, as brown, glistening, prismatic crystals; the trans-*bromide*, YBr_2, as thick, short, columnar or tabular, dark brown crystals; the trans-*thiocyanate*, $Y(SCN)_2$, as thick, glistening, brownish-yellow plates; the trans-*dithionate*,

$$YS_2O_6,H_2O,$$

as long, glistening, fluted prisms. This latter salt was also obtained from a solution of the *trans*-chloride, prepared by the interaction of 1 : 6-chloronitrodiethylenediaminecobaltic chloride and liquid ammonia.

The solubilities of the various *trans*-salts, expressed in grams of salt per 10 c.c. of water at 27°, are: nitrate, 2·827; thiocyanate, 1·458; bromide (at 26°), 0·6867; iodide, 0·7707.

Nitroisothiocyanatodiethylenediaminecobaltic salts, YX, where $Y = \left[\begin{matrix} O_2N \\ SCN \end{matrix} \text{Co en}_2\right]$.—The salts of the *trans*-series are more easily soluble than the *cis*-isomerides, the sulphates showing the greatest difference in solubility. There is also a marked difference in the colour of the salts, the *cis*-compounds being brownish-yellow, whilst the *trans*-compounds are dark brown.

The following reactions are different in the two series. Hydrogen peroxide partly oxidises the *cis*-salts to *cis*-nitroammine-salts, and partly oxidises the thiocyanate group completely away; the *trans*-salts, under similar conditions, give only *trans*-nitroaquo-salts, the thiocyanate group being split off completely. On heating with concentrated hydrochloric acid, the *cis*-isomerides give the *cis*-chloro*iso*thiocyanato-salts, whereas the *trans*-isomerides are not affected by the same treatment. On oxidation with nitric acid and subsequent evaporation with hydrochloric acid, the *cis*-salts give 1 : 6-dichloro-salts, whilst the *trans*-salts give 1 : 6-chloronitro-salts.

[With C. Rix.]—The cis-*chloride*, YCl,H_2O, is obtained by intramolecular transformation from 1 : 2-chloronitrodiethylenediamine-cobaltic thiocyanate, a solution of which in water containing acetic acid is evaporated to half its volume. The red colour changes to brown, and on cooling brownish-yellow needles of the *cis*-chloride deposit containing $2H_2O$, but $1H_2O$ is lost in a desiccator over calcium chloride. The chloride serves for the preparation of the other salts, for the most part by the method of double decomposition. The cis-*bromide*, YBr, forms light brown, nodular crystals; the cis-*iodide*, YI, crystallises in brown prisms; the cis-*sulphate*, Y_2SO_4, forms yellow, glistening scales; the cis-*nitrate*, YNO_3, forms brown, thick crystals; and the cis-*thiocyanate*, YSCN, crystallises in brown leaflets. The *cis*-sulphate may also be obtained by heating a solution of *cis*-chloro*iso*thiocyanato-diethylenediaminecobaltic chloride with sodium nitrite and subsequent precipitation with ammonium sulphate. The *cis*-thiocyanate is also prepared by heating a solution of the *cis*-chloronitro-chloride with potassium thiocyanate.

[With N. Goslings.]—The trans-*thiocyanate*, YSCN, is obtained as

brown, prismatic crystals when potassium thiocyanate is added to a solution of 1 : 6-chloronitrodiethylenediaminecobaltic nitrate. Methods are also described for its preparation by the action of potassium thiocyanate on nitratonitrodiethylenediaminecobaltic thiocyanate and on 1 : 6-nitroamminediethylenediaminecobaltic nitrate. The trans-*chloride*, YCl,H_2O, is obtained as reddish-brown, tabular crystals by dissolving the thiocyanate in concentrated hydrochloric acid and precipitation with alcohol; the other salts are prepared from it by appropriate double decomposition. The trans-*bromide*, YBr,H_2O, forms brown, tabular crystals; the trans-*iodide*, YI, crystallises in glistening, brown, irregular leaflets; the trans-*nitrate*, YNO_3,H_2O, forms brown plates, as also does the trans-*nitrite*, YNO_2,H_2O. With silver nitrate the *trans*-nitrate gives long, yellow needles of an *additive compound*, $\left[\begin{matrix}AgSCN\\ O_2N\end{matrix}\ Co\ en_2\right](NO_3)_2$.

Dinitrotetramminecobaltic salts, YX, where $Y=[(NO_2)_2Co(NH_3)_4]$.—[With L. Cohn.]—By the addition of rubidium nitrate to a solution of the *cis*-nitrate (flavonitrate), a *rubidium double nitrate*, $YNO_3,RbNO_3$, is obtained as brown, rhombic, tabular crystals. It is analogous with the potassium double nitrate already prepared by Jörgensen.

Dinitrodiethylenediaminecobaltic salts, YX, where

$$Y=[(O_2N)_2\ Co\ en_2].$$

—A number of the stereoisomerides have been described previously as dinitrito-salts (Abstr., 1901, i, 511); the true dinitrito-salts were prepared later (Abstr., 1907, i, 291). It has been found that the *cis*-nitrate is transformed into the *trans*-nitrate when its aqueous solution is heated. The cis-*thiocyanate*, YSCN, is obtained from the *cis*-nitrate by precipitation with potassium thiocyanate; it forms glistening, yellowish-brown, tabular crystals. The trans-*thiocyanate*, YSCN, forms orange-yellow, glistening, thick crystals. The trans-*hydrogen sulphate*, $YHSO_4$, has been prepared from the iodide by interaction with silver oxide and subsequent neutralisation with sulphuric acid; it forms glistening, yellowish-red needles.

Stereoisomeric *chloronitrodiethylenediaminecobaltic* salts,

$$\left[\begin{matrix}Cl\\ O_2N\end{matrix}\ Co\ en_2\right]X,$$

have already been described (Abstr., 1901, i, 512). It has since been found that the *trans*-salts can be exposed to the action of concentrated hydrochloric acid for a long time without effect, whilst the *cis*-salts rapidly give 1 : 2- and 1 : 6-dichloro-salts.

trans-*Nitronitratodiethylenediaminecobaltic* salts, YX, where $Y=\left[\begin{matrix}O_2N\\ O_3N\end{matrix}\ Co\ en_2\right]$.—Only the *nitrate*, YNO_3, has been obtained. It is prepared by the oxidation of 1 : 2-dinitrodiethylenediaminecobaltic nitrate with concentrated nitric acid, and forms glistening, chamois-coloured crystals. By precipitation of the aqueous solution with concentrated nitric acid, an *acid nitrate*, YNO_3,HNO_3, is obtained.

trans-*Nitroaquodiethylenediaminecobaltic* salts, YX_2, where $Y=\left[\begin{matrix}O_2N\\ H_2O\end{matrix}\ Co\ en_2\right]$.—The *sulphate*, YSO_4, is obtained as follows: 2·8 grams of solid ammonium sulphate are added to a solution of 4 grams

of 1 : 6-nitronitrato-diethylenediaminecobaltic nitrate in 10 c.c. of water, and then alcohol added until no further precipitate forms. It crystallises in orange-coloured needles. No other salts could be obtained, owing to their great solubility.

Dichloroethylenediaminediamminecobaltic salts, YX, where

$$Y = \left[Cl_2Co \begin{matrix} (NH_3)_2 \\ en \end{matrix} \right].$$

—Both series of stereoisomerides have been obtained. The method of preparation is briefly as follows: By warming trinitrotriamminecobalt with ethylenediamine, trinitroethylenediamineamminecobalt is obtained

$$(NO_2)_3Co(NH_3)_3 + en = (NO_2)_3Co \begin{matrix} en \\ NH_3 \end{matrix} + 2NH_3.$$

By heating with concentrated hydrochloric acid, the latter salt is transformed into dichloroaquoethylenediamineamminecobaltic chloride, $\left[\begin{matrix} Cl_2 \\ H_2O \end{matrix} Co \begin{matrix} en \\ NH_3 \end{matrix} \right]Cl$, of which 1 gram is then dissolved in 25% ammonia ($3\frac{1}{2}$ c.c.). After five minutes, 3·5 c.c. of concentrated hydrochloric acid are added to the solution, which is then heated until it becomes greenish-blue in colour. On cooling, green crystals of the trans-*chloride*, $YCl,\frac{1}{2}H_2O$, are deposited, from which, by the method of double decomposition, the following salts were obtained, generally as green precipitates: trans-*nitrate*, YNO_3; trans-*iodide*, YI; trans-*bromide*, YBr; trans-*thiocyanate*, YSCN; trans-*hydrogen sulphate*, $YHSO_4,H_2O$; trans-*dithionate*, $Y_2S_2O_6$. The iodide is sensitive to light.

The *cis*-isomerides were prepared from the *trans*-compounds as follows: By heating a solution of the *trans*-chloride with potassium carbonate until the colour had changed to red, and then cooling, garnet-red crystals of *carbonatoethylenediaminediamminecobaltic chloride*,

$$\left[CO_3Co \begin{matrix} en \\ (NH_3)_2 \end{matrix} \right]Cl,$$

were obtained. By treating this compound with concentrated hydrochloric acid in the cold, a solution of the required *cis*-chloride was obtained, from which, on the addition of ammonium bromide, the cis-*bromide*, YBr, was deposited as a bluish-violet precipitate. The cis-*dithionate*, $Y_2S_2O_6$, is a violet precipitate obtained from a solution of the bromide by the addition of sodium dithionate.

[With G. Lindenberg.]—*Diacidoditrimethylenediaminecobaltic* salts, $[X_2Co\,(tn)_2]X$.—Only the 1 : 6-dinitro- and 1 : 6-dichloro-salts have so far been prepared. The 1 : 6-dichloro-salts are distinguished from the corresponding diethylenediamine salts by their ready hydration (formation of aquo-salts) in aqueous solution. The neutral, green solution of a dichloroditrimethylenediamine salt rapidly becomes violet in colour; the addition of concentrated hydrochloric acid restores the green colour.

Carbonato-salts have been prepared from the 1 : 6-dichloro-salts, but could not be made to furnish the stereoisomeric 1 : 2-dichloro-salts.

trans-*Dinitroditrimethylenediaminecobaltic* salts, YX, where

$$Y = [(NO_2)_2\ Co\,tn_2].$$

—The *nitrite*, YNO_2, is obtained by heating potassium cobaltinitrite with trimethylenediamine in aqueous solution. It forms large, thick, yellowish-brown, pleochroic, rhombic crystals. The *bromide*,

$$YBr,H_2O,$$

and the *iodide*, $YI,2H_2O$, are obtained from the nitrite by interaction with potassium bromide and iodide respectively, the former as brownish-yellow, monoclinic crystals, and the latter as yellow to yellowish-green, pleochroic, rhombic prisms. The *chloride*, YCl,H_2O, and *nitrate*, YNO_3, are best obtained from the iodide by interaction with silver chloride and nitrate respectively; the former gives light to dark brown, pleochroic, monoclinic crystals, and the latter rhombic plates.

1 : 6-*Dichloroditrimethylenediaminecobaltic chloride*, $[Cl_2\,Co\,tn_2]Cl$, is obtained by heating the dinitronitrite with hydrochloric acid; a green solution is obtained, which, on cooling, deposits green, prismatic, columnar crystals. The solution is turned red by sodium hydroxide and ammonia, and gives characteristic precipitates with the bromide, iodide, thiocyanate, permanganate, ferrocyanide, ferricyanide, or nitrate of potassium, and with sodium thiosulphate. Hydrogen sulphide precipitates cobalt sulphide. Potassium platinichloride gives green crystals of the *platinichloride*, $[Cl_2\,Co\,tn_2]_2PtCl_6$.

Carbonatoditrimethylenediaminecobaltic chloride, $[CO_3\,Co\,tn_2]Cl,H_2O$, was obtained by heating a solution of the 1 : 6-dichloro-chloride with sodium carbonate until it became bluish-red in colour. The addition of alcohol precipitated a white salt, and the red solution remaining deposited the required chloride in red, needle-shaped crystals. By interaction with hydrogen chloride, no matter under what conditions, the green 1 : 6-dichloro-chloride was always obtained. T. S. P.

Optically-active Compounds of Cobalt and Chromium.

ALFRED WERNER (*Arch. Sci. Phys. Nat.*, 1911, [iv], 32, 457—467).—A general account is given of results which have, for the most part, been already published (Abstr., 1911, i, 613, 838, 960; this vol., i, 10). In addition, the author mentions that optically-active compounds of the *tetraethylenediamine-μ-aminoperoxodicobalt* and *tetraethylenediamine-μ-amino-ol-dicobalt* series have been obtained. The rotations of the compounds of the first series are very large, the nitrate of the first series having a specific rotation of 840°, which corresponds with a molecular rotation of about 6000°.

From a consideration of the results hitherto obtained it follows that the sign of the rotation is not connected with the configuration of the diethylenediaminecobaltic radicle. This is well shown by the fact that *l*-tetraethylenediamine-μ-aminoperoxodicobalt salts furnish *d*-tetraethylenediamine-μ-amino-ol-dicobalt salts on reduction:

$$\left[en_2\overset{\text{IV}}{Co}\begin{matrix}\cdot NH_2\cdot\\ \cdot O_2\cdot\end{matrix}\overset{\text{III}}{Co}\,en_2\right]X_4 \longrightarrow \left[en_2\,Co\begin{matrix}\cdot NH_2\cdot\\ \cdot OH\cdot\end{matrix}Co\,en_2\right]X_4.$$

Also, *l*-chloro*iso*thiocyanatodiethylenediaminecobaltic salts and *d*-chloronitrodiethylenediaminecobaltic salts both give rise to *d*-nitro*iso*thiocyanatodiethylenediaminecobaltic salts by interaction with sodium nitrite and potassium thiocyanate respectively.

An examination of the compounds hitherto prepared shows that it is not always the isomeride of the same sign of rotation which gives the least soluble salt with *d*-bromocamphorsulphonic acid.

T. S. P.

Preparation of Acid Chlorides from Two or More Molecules of Carbamide Chloride by Elimination of Hydrogen Chloride. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 238961).—When carbamide chloride is heated in the absence of moisture either with or without a solvent, two or more molecules condense with evolution of hydrogen chloride.

Allophanic chloride, $NH_2\cdot CO\cdot NH\cdot COCl$, a fuming, colourless, readily decomposable powder, which reacts energetically with water according to the equation: $NH_2\cdot CO\cdot NH\cdot COCl + H_2O = CO(NH_2)_2 + CO_2 + HCl$, was thus obtained at 30°, whilst at about 100° three molecules combined, yielding *biuretcarboxyl chloride*, $C_2H_4N_3O_2\cdot COCl$, a colourless, non-fuming powder, decomposed by water with elimination of hydrogen chloride and carbon dioxide: $C_2H_4O_2N_3\cdot COCl + H_2O = HCl + CO_2 + NH_2\cdot CO\cdot NH\cdot CO\cdot NH_2$.

F. M. G. M.

Hypochlorous [Acid and] Amides. ÉTIENNE BOISMENU (*Compt. rend.*, 1912, **154**, 1482—1484. Compare Abstr., 1911, i, 957).—The action of an aqueous solution of hypochlorous acid on amides at 0° gives rise to monochloro- or dichloro-amides, according to the proportion of amide and of water employed. The dichloro-derivatives are yellow liquids, the stability of which diminishes as the molecular weight increases. On treatment with amides, they yield monochloro-derivatives.

Acetyldichloroamide, $CH_3\cdot CO\cdot NCl_2$, has an odour of chlorine, and is insoluble in water. It decomposes above 0°, depositing crystals of acetylchloroamide. *Propionyldichloroamide* and *formyldichloroamide* have also been prepared. The latter is very explosive, and must be kept in well cooled vessels (compare Mauguin, Abstr., 1909, i, 892).

W. O. W.

Cobalt Thiocyanates, and the Cause of the Colour Changes in Cobalt Salts. ARTHUR HANTZSCH and YUJI SHIBATA (*Zeitsch. anorg. Chem.*, 1912, **73**, 309—324).—Cobaltous thiocyanate is largely bimolecular in urethane solution at 49°, but almost completely unimolecular in alcoholic solution at 78°. The existence of complex ions in the alcoholic solution is shown by the method used by Donnan and Bassett (Trans., 1902, **81**, 944). The absorption spectra show the blue cobalt band, and a broad band in the ultra-violet with its maximum at $1/\lambda$ 3400 and minimum at $1/\lambda$ 3850. The absorption is slightly increased at 55° and 80°. Beer's law is departed from at considerable dilutions.

The colour of the blue solution is attributed to the presence of the complex salt, $Co(SCN)_4Co$, in confirmation of which it is noted that the compound, $Co(SCN_4)Me_2$, is blue. The salt, $Co(SCN)_4K_2$, is blue, but its spectrum in absolute alcohol is practically identical with that of cobalt thiocyanate, indicating dissociation into its components. Amyl alcohol gives an almost identical solution, whilst moist ether

contains the salt in an almost undissociated condition. The action of alcohols in promoting dissociation is attributed to the formation of the known alcoholates of cobalt thiocyanate. The decomposition is still more pronounced in aqueous solution, but is lessened by the addition of potassium thiocyanate.

The blue colour of cobalt thiocyanate is changed to pink by the addition of mercuric chloride or zinc chloride. The colour of the salt, $Co(SCN)_2,HgCl_2$, is not altered by further addition of mercuric chloride. This salt has not been isolated, but when the alcoholic solution is evaporated with a further quantity of mercuric chloride, pink crystals of a compound, $2Co(SCN)_2,3HgCl_2$, are obtained. The change of colour in cobalt chloride solution is also due to the formation of a compound, $[CoCl_4,(HgCl_2)_2]Co$, and not, as assumed by Donnan and Bassett, to $(HgCl_4)Co$.

The molecular weight of cobalt thiocyanate in aqueous solution shows that it only dissociates into two ions, except in very dilute solutions, whilst the chloride and bromide yield three ions, even in concentrated solutions. It is therefore considered to exist in solution as the compound $\left[Co^{(SCN)}_{(H_2O)_5}\right]SCN$. The whole of the colour changes may be explained as changes of the co-ordinative unsaturated complex, CoX_4, into the saturated complex, CoX_6. C. H. D.

Systems Formed by Antimony Chloride and Bromide with Monosubstituted Benzene Hydrocarbons. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1275—1302. Compare Abstr., 1911, i, 273).—The author has subjected to thermal analysis the systems formed by antimony chloride and bromide with toluene, ethylbenzene, propylbenzene (see Abstr., 1911, i, 532), and *iso*amylbenzene. The results are given in the form both of curves and of tables.

Rosenheim and Stellmann (Abstr., 1902, i, 68) state that antimony trichloride forms with toluene a compound having a composition analogous to that of the benzene compound, namely, $3SbCl_3,C_6H_5Me$; but this compound is really $2SbCl_3,C_6H_5Me$, the solid phase corresponding with $3SbCl_3$, C_6H_5Me being antimony trichloride itself.

The melting points of the thirteen compounds formed by the eight systems examined are as follows:

	$2SbCl_3,C_6H_5R$.	$SbCl_3,C_6H_5R$.	$2SbBr_3,C_6H_5R$.	$SbBr_3,C_6H_5R$.
SbX_3–C_6H_5Me	42·5°	15—16° (decomp.)	38—39° (decomp.)	9° (decomp.)
SbX_3–C_6H_5Et	37·0	39·0°	—	33 ,,
SbX_3–C_6H_5Pr	9—10 (decomp.)	1·5	—	1 ,,
SbX_3–$C_6H_5·C_5H_{11}$ ...	7·5° (decomp.)	−20·5	—	−15 ,,

It will be seen that increase of the magnitude of the benzene substituent is accompanied by decrease in the stability of the compounds formed with antimony trichloride and tribromide.

The transition (p) and eutectic (e) points, and the corresponding

compositions (mols. of hydrocarbon per mol. of antimony chloride), are given in the following table:

	$2SbCl_3,C_6H_5R$–$SbCl_3,C_6H_5R$.		$2SbCl_3,C_6H_5R$–$SbCl_3$.		$SbCl_3,C_6H_5R$–$SbCl_3$.	
	Temp.	Composition.	Temp.	Composition.	Temp.	Composition.
$SbCl_3$–C_6H_5Me ..	11°	1·8 (*p*)	40·0°	0·46 (*e*)	—	—
$SbCl_3$–C_6H_5Et......	35	0·62 (*e*)	36·8	0·47 (*e*)	33°	0·52 (*e*)
$SbCl_3$–C_6H_5Pr......	—	—	8·5	0·88 (*p*)	1	0·98 (*e*)
$SbCl_3$–$C_6H_5{\cdot}C_5H_{11}$.	−33	3·1 (*p*)	−21·0	1·3 (*p*)	−5	1·2 (*p*)

The transition points for $SbBr_3,C_6H_5R$–$SbBr_3$ are as follows:

	Temp.	Composition.
$SbBr_3$–C_6H_5Me	—	—
$SbBr_3$–C_6H_5Et	29°	1·17
$SbBr_3$–C_6H_5Pr	−5	3·1
$SbBr_3$–$C_6H_5{\cdot}C_5H_{11}$	−17	5·07

This continual fall in the transition temperature again indicates diminution of stability of these compounds as the magnitude of the hydrocarbon increases. T. H. P.

Systems Formed by Antimony Trichloride and Tribromide with Disubstituted Benzene Hydrocarbons. Boris N. Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1303—1328).—The systems here described contain *o*-, *m*-, or *p*-xylene or *p*-cymene. The results of the thermal analyses are given as curves and tables.

The replacement of a second hydrogen atom of benzene by an alkyl radicle (compare preceding abstract) produces no change in the character of the system, the temperature diagrams being similar to those given by the systems containing monosubstituted benzenes. Also, here too, antimony chloride gives compounds of the two types $2SbCl_3,C_6H_4R_2$ and $SbCl_3,C_6H_4R_2$, whilst the bromide, as a rule, yields only one compound, $SbBr_3,C_6H_4R_2$. The compounds are of approximately the same stability as those formed with toluene or ethylbenzene. The results obtained with the three xylenes show that isomerism exerts a marked influence on the physical properties of these compounds.

The melting points of the hydrocarbons and of the various compounds they form are given below, the numbers for methylbenzene being inserted for purposes of comparison:

	Hydro-carbon.	$2SbX_3,C_6H_4R_2$.	Diff.	$SbX_3,C_6H_4R_2$.	Diff.
$SbCl_3$–*p*-$C_6H_4Me_2$	14°	70°	56°	56°	42°
$SbCl_3$–*m*-$C_6H_4Me_2$......	−57	38	95	7·5 (decomp.)	64·5
$SbCl_3$–*o*-$C_6H_4Me_2$	−29	33·5	62·5	19·5°	48·5
$SbCl_3$–C_6H_5Et	−93	37	130	39	132
$SbCl_3$–*p*-$C_6H_4MePr^{\beta}$ ...	−75	40	115	5—6 (decomp.)	80
$SbBr_3$–*p*-$C_6H_4Me_2$......	14	67·5	53·5	—	—
$SbBr_3$–*m*-$C_6H_4Me_2$ ...	−57	—	—	13·5	70·5
$SbBr_3$–*o*-$C_6H_4Me_2$......	−29	—	—	24	53
$SbBr_3$–C_6H_5Et	−93	—	—	33 (decomp.)	126
$SbBr_3$–*p*-$C_6H_4MePr^{\beta}$ ..	−75	—	—	10 (decomp.)	85

T. H. P.

Relations of Trisubstituted Benzene Hydrocarbons to Antimony Trichloride and Tribromide. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1329—1341).—The systems formed by antimony trichloride and tribromide with 1 : 3 : 5- and 1 : 2 : 4-trimethylbenzenes (mesitylene and ψ-cumene) have been examined.

Mesitylene forms compounds of the two types $2SbX_3,C_6H_3Me_3$ and $SbX_3,C_6H_3Me_3$ with both antimony chloride and bromide, and the same is the case with ψ-cumene. The only other benzene hydrocarbon with which this has been found to occur is toluene.

The melting points of these compounds are as follows:

	$2SbX_3,C_6H_3Me_3$.	$SbX_3,C_6H_3Me_3$.
$SbCl_3$–1 : 3 : 5-$C_6H_3Me_3$	75·5°	43° (decomp.)
$SbCl_3$–1 : 2 : 4-$C_6H_3Me_3$	56·0	– 4 to – 5° ,,
$SbBr_3$–1 : 3 : 5-$C_6H_3Me_3$	69·5	38—39 ,,
$SbBr_3$–1 : 2 : 4-$C_6H_3Me_3$	36·0 (decomp.)	13 ,,

The eutectic points and the corresponding compositions are as follows:

System ...	(1) $C_6H_3Me_3$–$SbX_3,C_6H_3Me_3$.			(2) $2SbX_3,C_6H_3Me_3$–SbX_3.		
	Temp.	Composition.	M. p. of hydrocarbon.	Temp.	Composition.	M. p. of SbX_3.
$SbCl_3$–1 : 3 : 5-$C_6H_3Me_3$	– 55·6°	126·2	– 54·4°	58·5°	0·15	73°
$SbCl_3$–1 : 2 : 4-$C_6H_3Me_3$	– 60·0	8·25	– 57·4	51·0	0·27	73
$SbBr_3$–1 : 3 : 5-$C_6H_3Me_3$	– 55·2	147·0	– 54·4	69·0	0·42	94
$SbBr_3$–1 : 2 : 4-$C_6H_3Me_3$	– 58·8	28·4	– 57·4	—	—	—

(The composition is given in mols. of hydrocarbon per mol. of SbX_3.)

The transition points, $SbX_3,C_6H_3Me_3$–$2SbX_3,C_6H_3Me_3$, are as follows:

	Temp.	Composition.
$SbCl_3$–1 : 3 : 5-$C_6H_3Me_3$	38°	1·8
$SbCl_3$–1 : 2 : 4-$C_6H_3Me_3$	– 5	1·83
$SbBr_3$–1 : 3 : 5-$C_6H_3Me_3$	29	3·45
$SbBr_3$–1 : 2 : 4-$C_6H_3Me_3$	7	1·72

Increase of the number of hydrogen atoms of benzene replaced by alkyl radicles does not diminish, but rather increases, the capability of these hydrocarbons to form compounds with antimony trichloride and tribromide. T. H. P.

Electrolytic Reduction of Nitrobenzene. RALPH CUTHBERT SNOWDON (*J. Physical Chem.*, 1911, **15**, 797—844).—The author endeavoured to develop an electrolytic method of reducing nitrobenzene which should not require the use of a porous cup or a platinum anode.

Nitrobenzene was vigorously stirred with ferrous chloride solution at 100° in a long cell provided with iron electrodes. The amount of anode iron dissolved was largely in excess of the electrolytic equivalent, and dissolution of iron also occurred at the cathode in increasing proportion as the current density was lowered. With high current densities (10 amp./dm^2), cathode corrosion was very small, and the

yield attained 95% of aniline on the total iron dissolved. Although sheet iron in ferrous chloride solution will not reduce nitrobenzene on boiling, it was found that under the emulsifying influence of rapid stirring the iron electrodes dissolved equally, without electrolytic aid, and gave a 78% yield of aniline calculated on the iron dissolved, so that the commercial reduction of nitrobenzene by massive iron might be rendered possible by suitable agitation to bring the substances into intimate contact. The presence of a dissolved ferrous salt is essential in the electrolytic as in the chemical reduction. Ferrous chloride is apparently without action on nitrobenzene, so that its catalytic activity must be attributed to a depolarising influence on the iron. In this respect ferrous chloride and acetate are more efficient than the sulphate and benzoate.

Nitrobenzene is reduced at 100° by alkaline sodium sulphide, freshly precipitated ferrous hydroxide, and sodium arsenite, but not by alkaline potassium ferrocyanide.

Sodium arsenite gives 60—90% of azoxybenzene, 5—14% of aniline, and a trace of azobenzene. This is contrary to electrolytic experience where azobenzene is produced above and azoxybenzene below 90°. Alkaline sodium sulphide and ferrous hydroxide give aniline and small amounts of azobenzene. The yield appears to vary with the order in which the three components, nitrobenzene, sodium hydroxide, and reducing agent, are mixed. R. J. C.

Aromatic Nitro-derivatives. Roberto Ciusa (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 523—524. Compare Abstr., 1911, i, 931).—The observation of Werner (Abstr., 1910, i, 20) that trinitromesitylene gives yellow solutions in some organic solvents, although it is not dissociated in formic acid solution, indicates that there is no connexion between the dissociability of the aromatic nitro-derivatives and their power to form additive products. The author now finds that tetranitromethane also is not dissociated in formic acid solution, although it can form additive products. R. V. S.

Isomorphous Mixtures: the Systems Chloronitrobenzenes–Bromonitrobenzenes. Robert Kremann (*Zeitsch. Kryst. Min.*, 1911, 50, 86; from *Jahrb. k.k. geol. Reichs.*, 1908, 58, 659—672).—The time-cooling curves and the freezing curves of the three systems (ortho, meta, para) show that the crystallisation interval for mixtures of the ortho-series is very small; that of the meta-series is also small, but it is larger in the para-series. The fusion curves of the two last systems belong to Roozeboom's type V. L. J. S.

1-Bromo-2:4:6-tri-iodo-3:5-dinitrobenzene and Some of its Derivatives. C. Loring Jackson and Harold E. Bigelow (*Amer. Chem. J.*, 1911, 46, 549—574).—It has been shown by Jackson and Robinson (Abstr., 1890, 377) that 1:3:5-tribromo-4:6-dinitrobenzene is converted by ethyl sodiomalonate into ethyl 3-bromo-4:6-dinitrophenylmalonate. It has now been found that when 1-bromo-2:4:6-tri-iodo-3:5-dinitrobenzene is treated with ethyl sodiomalonate at the ordinary temperature, 1-bromo-2:6-di-iodo-3:5-dinitrobenzene and ethyl ethanetetracarboxylate are produced, whilst if the mixture is

heated, ethyl 2-bromo-3-iodo-4 : 6-dinitrophenylmalonate is obtained. This shows that the explanation given previously (Jackson and Moore, Abstr., 1890, 497; Jackson, Abstr., 1890, 983) is not correct, but that it must be assumed that ethyl sodiomalonate reacts in the enolic form, and that the iodine atom and the $\cdot C_6BrI_2(NO_2)_2$ group are added at the double bond with production of the compound

$$CO_2Et\cdot CHI\cdot C(OEt)(ONa)\cdot C_6I_2Br(NO_2)_2.$$

On acidification, the hydrogen of the ·OH group might combine with the substituted phenyl group with formation of the compounds $C_6HBrI_2(NO_2)_2$ and $CHI(CO_2Et)_2$; the latter would then react with the excess of ethyl sodiomalonate to produce ethyl ethanetetracarboxylate.

1-*Bromo*-2 : 4 : 6-*tri-iodobenzene*, $C_6H_2BrI_3$, m. p. 146°, obtained by treating a mixture of 2 : 4 : 6-tri-iodoaniline, glacial acetic acid, and hydrobromic acid with sodium nitrite, crystallises in pale yellow needles, and when heated with fuming nitric acid is converted into 1-*bromo*-2 : 4 : 6-*tri-iodo*-3 : 5-*dinitrobenzene*, $C_6BrI_3(NO_2)_2$, m. p. 292°, which forms white needles. When tri-iodoaniline containing dark-coloured impurities was employed, the crude 1-bromo-2 : 4 : 6-tri-iodobenzene yielded, on nitration, some 1 : 3-*dibromo*-2:4:6-*tri-iodo*-5-*nitrobenzene*, $C_6Br_2I_3\cdot NO_2$, m. p. about 256° (decomp.), which crystallises in hexagonal prisms.

1-*Bromo*-2 : 6-*di-iodo*-3 : 5-*dinitrobenzene*, $C_6HBrI_2(NO_2)_2$, m. p. 187°, crystallises in straw-coloured needles. *Ethyl* 2-*bromo*-3-*iodo*-4 : 6-*dinitrophenylmalonate*, $C_6HBrI(NO_2)_2\cdot CH(CO_2Et)_2$, m. p. 107°, forms stout, lemon-yellow crystals. A small quantity of another *compound*, m. p. about 250° (decomp.), was also isolated from the product of the reaction between ethyl sodiomalonate and 1-bromo-2 : 4 : 6-tri-iodo-3 : 5-dinitrobenzene.

By the action of sodium ethoxide on 1-bromo-2 : 4 : 6-tri-iodo-3 : 5-dinitrobenzene, 3-*bromo*-2 : 4 : 6-*tri-iodo*-5-*nitrophenetole*,

$$C_6BrI_3(NO_2)\cdot OEt,$$

m. p. 148°, is obtained, which crystallises in light pink needles, and is reduced by zinc and acetic acid to *m*-aminophenol. 3-*Bromo*-2:4:6-*tri-iodo*-5-*nitroanisole*, $C_6BrI_3(NO_2)\cdot OMe$, m. p. 163°, forms pale yellow needles.

When 2-bromo-1:3:5-tri-iodo-4:6-dinitrobenzene is heated with zinc and acetic acid, 5-bromo-*m*-phenylenediamine is produced, but on reduction with ferrous hydroxide it is converted into 1-*bromo*-2 : 4 : 6-*tri-iodo*-m-*phenylenediamine*, $C_6BrI_3(NH_2)_2$, m. p. 187°, which forms stout, greyish-white needles, and yields a *hydrochloride*, decomposing at 100°.

Reduction experiments have been carried out with several other iodo-compounds. Zinc and acetic acid remove iodine from 1 : 3 : 5-tri-iodo-4 : 6-dinitrobenzene. 2 : 4 : 6-Tri-iodoaniline is not affected by tin and hydrochloric acid, and only very slightly by zinc and acetic acid. 1-Bromo-2 : 4 : 6-tri-iodobenzene is reduced by zinc and acetic acid with formation of *p*-iodobromobenzene. These experiments show that iodine is more easily replaced by hydrogen than is bromine.

Sodium ethoxide does not react with 2 : 4 : 6-tri-iodobenzene, and only very slightly with 1-bromo-2 : 4 : 6-tri-iodobenzene. E. G.

Preparation of Alkylamines by Catalysis. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, **153**, 1204—1208. Compare Abstr., 1909, i, 292; 1911, ii, 627).—An extension of the general reaction already described to the preparation of new amines.

*iso*Propyl alcohol is transformed into *iso*propylamine when its vapour mixed with ammonia is passed over thorium dioxide at 250°; the yield is 20%. At higher temperatures propylene is formed together with di*iso*propylamine. The reaction proceeds with difficulty in the case of diphenylcarbinol. At 280° the corresponding amine is obtained, but the chief product is tetraphenylethylene; this substance is easily obtained at 300° in absence of ammonia.

*cyclo*Hexanol and also its 2-, 3-, and 4-methyl derivatives yield the primary and secondary amines at 290—320°. 4′-*Methyl*cyclo*hexylamino*-4-*methyl*cyclo*hexane*, $(C_6H_{10}Me)_2NH$, b. p. 275° (decomp.), forms a *phenylcarbamide*, m. p. 181°.

The following secondary amines were prepared by passing a mixture of *cyclo*hexylamine and an alcohol over thorium dioxide at 320°. Ethylamino*cyclo*hexane, $C_6H_{11}\cdot NHEt$. *Propylamino*cyclo*hexane*, b. p. 185°; the *phenylcarbamide* has m. p. 113°. iso*Butylamino*cyclo*hexane*, b. p. 193°; the *phenylcarbamide* has m. p. 90°. iso*Amylamino*cyclo*hexane*, b. p. 205°; the *phenylcarbamide* has m. p. 129°. *Benzylamino*cyclo*hexane*, b. p. 195°/80 mm., the *phenylcarbamide* has m. p. 121°.

cyclo*Hexylamino-2-methyl*cyclo*hexane*, b. p. 260° with slight decomposition; the *hydrochloride* has m. p. 182°, and the *phenylcarbamide*, m. p. 140°; the 3-*methyl* derivative, b. p. 270° (decomp.), forms a *hydrochloride*, m. p. 197°, and a *phenylcarbamide*, m. p. 191°, whilst the 4-*methyl* derivative, b. p. 270°, gives a *phenylcarbamide*, m. p. 108°. The yield of the latter was 20%; the lowest yield was obtained in the case of *methylamino*cyclo*hexane*. W. O. W.

Behaviour of Nitrosomonoarylcarbamides towards Primary Amines and Phenols. J. HAAGER (*Monatsh*, 1911, **32**, 1089—1102). —Nitrosomonoarylcarbamides condense in alcoholic solution with primary aromatic bases to diazoamino-compounds, which contain the aromatic nuclei of both components, and to arylcarbamides which contain the nuclei of the bases. Accordingly, the rest of the carbamic acid, and not the nitroso-group, is eliminated from the nitrosocarbamides. The change is the same when the mixture of the components is heated.

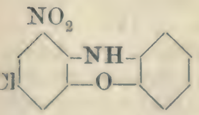
Nitrosoarylcarbamides react also with alkaline, and with alcoholic, solutions of phenols and their derivatives, with the formation of, hydroxyazo-compounds and alkaline salts of cyanic acid, which have been formed by the elimination of $-CO\cdot NH_2$ from the nitrosocarbamides.

Nitrosophenylcarbamide reacts with aniline to form diazoaminobenzene and phenylcarbamide; with *p*-toluidine, benzenediazoaminotoluene, m. p. 85°, and *p*-tolylcarbamide are obtained. Nitroso-*p*-tolylcarbamide and aniline yield the same compounds.

Nitrosocarbamide with phenol yields benzeneazophenol; with resorcinol it gives benzeneazoresorcinol, m. p. 161°. *p*-Nitrosotolylcarbamide and resorcinol give rise to *p*-tolueneazoresorcinol, m. p. 183—184°. E. F. A.

The Action of Phosphorus Thiochloride on Alkaline Solutions of Phenols. WILHELM AUTENRIETH (*Ber.*, 1911, **44**, 3754—3755).—The author draws attention to the fact that several of the substances prepared previously by himself (Abstr., 1898, i, 419) have since been described afresh with different nomenclature (Ephraim, Abstr., 1911, i, 284; this vol., i, 26). D. F. T.

Dinitrophenols. FRITZ ULLMANN and SHRIRANG M. SANÉ (*Ber.*, 1911, **44**, 3730—3737. Compare Abstr., 1908, i, 525; 1909, i, 21, 23).—On warming 4-chloro-2 : 6-dinitrophenol with toluenesulphonyl chloride and diethylaniline, 1 : 4-*dichloro*-2 : 6-*dinitrobenzene* is obtained; it forms colourless leaflets, m. p. 105° (corr.). If, however, the diethylaniline is replaced by sodium carbonate solution, the product is 4-*chloro*-2 : 6-*dinitrophenyl* p-*toluenesulphonate*; this crystallises in colourless needles, m. p. 127° (corr.); the action of ammonia on a boiling xylene solution of this ester yields 4-chloro-2 : 6-dinitroaniline (compare Körner, Abstr., 1876, i, 230); similarly, the action of aniline on an alcoholic solution of the ester produces orange-yellow needles of 4-*chloro*-2 : 6-*dinitrodiphenylamine*, m. p. 130°, the same substance being obtained also from aniline and 1 : 4-dichloro-2 : 6-dinitrobenzene. The last-named substance also reacts with dimethylamine, yielding 4-chloro-2 : 6-dinitrodimethylaniline as orange-yellow crystals, m. p. 111° (probably identical with that already described by Pinnow, Abstr., 1899, i, 203). By the action of the above-mentioned dichlorodinitrobenzene or chlorodinitrophenyl p-toluenesulphonate on o-aminophenol there is obtained 3-*chloro*-5-*nitrophenoxazine* (annexed formula) in violet needles, m. p. about 192°.



1 : 2-*Dichloro*-3 : 5-*dinitrobenzene* is obtained from 6-chloro-2 : 4-dinitrophenol in a similar manner to the 1 : 4-dichloro-isomeride above; it forms hexagonal, pale yellow tablets, m. p. 56°; in boiling alcoholic solution with ammonia it yields yellow needles of 2-*chloro*-4 : 6-*dinitroaniline* (m. p. 157°), and with aniline, brick-red crystals of 2-*chloro*-4 : 6-*dinitrodiphenylamine*. Heated in alcoholic solution with o-aminophenol, it yields 3 : 5-dinitrophenoxazine (compare Turpin, Trans., 1891, **59**, 722).

2-Chloro-3 : 5-dinitrotoluene, m. p. 63° (corr.), is obtained by the action of toluenesulphonyl chloride and diethylaniline on 3 : 5-dinitro-o-cresol; the lower m. p. previously obtained for this substance (Nietzki and Rehe, Abstr., 1893, i, 15) was due to impurity. In the above process, 3 : 5-*dinitro*-o-*tolyl* p-*toluenesulphonate* (colourless needles, m. p. 167°), is obtained as a by-product. If the above chlorodinitrotoluene is allowed to react with o-aminophenol, 2 : 4-*dinitro*-6-*methyl*-2′-*hydroxydiphenylamine* is obtained, which crystallises in reddish-brown tablets, m. p. 177° (corr.), and by treatment with dilute soda passes into 3-*nitro*-5-*methylphenoxazine* (brown needles, m. p. 205° with decomp.).

The methyl esters of 3 : 5-dinitro-2-hydroxybenzoic acid and of 3 : 5-dinitro-4-hydroxybenzoic acid on treatment with toluenesulphonyl chloride and diethylaniline give the methyl esters of 2-chloro-3 : 5-

dinitrobenzoic acid (compare Purgotti, Abstr., 1902, i, 777) and 4-chloro-3 : 5-dinitrobenzoic acid (compare Ullmann, Abstr., 1909, i, 475) respectively. D. F. T.

The Action of Metals on Fused Picric Acid. J. Saposhnikoff (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1911, 6, 183—185).—Kast's work is discussed (Abstr., 1911, i, 852). The author heated one gram of various metals (in shavings or powder) with two grams of picric acid at 125°; the amount of dissolved metal was estimated and found, with the exception of tin, to be in proportion to the equivalent weights of the metal. The respective weights dissolved by the picric acid were: tin, 0·00; aluminium, 0·0488; iron, 0·153; copper, 0·1754; nickel, 0·1862; zinc, 0·2046, and lead, 0·2798 gram. F. M. G. M.

Electrolytic Reduction of Nitrated Phenyl Thiocyanates. Fritz Fichter and Theodor Beck (*Ber.*, 1911, 44, 3636—3648).—Müller has shown that the reduction of *o*-nitrophenyl, *p*-nitrophenyl, and 2 : 4-dinitrophenyl thiocyanates by alcoholic ammonium sulphide causes elimination of the thiocyano-group and the formation of nitrated diphenyl disulphides, whilst their reduction by stannous chloride yields thiazole derivatives (*Zeit. Farb. Ind.*, 1906, 5, 357). The authors now show that different products are obtained by the electrolytic reduction of these thiocyanates at lead or copper cathodes; the thiocyano-group is only attacked when lead cathodes are used. The reduction of phenyl thiocyanate in 2*N*-alcoholic sulphuric acid at a rotating lead cathode and with a current density of 0·02 ampere per sq. cm. (the anodic compartment contains a lead plate in 2*N*-sulphuric acid) yields hydrogen cyanide and 57·5% of phenyl mercaptan. Under similar conditions the reduction of *o*-nitrophenyl thiocyanate yields 1-aminobenzthiazole, which is probably produced by the secondary interaction of the *o*-aminophenyl mercaptan and hydrogen cyanide initially formed. With a copper cathode and a current density of 0·019 ampere per sq. cm., *o*-nitrophenylthiocyanate is reduced to the *sulphate* of 2-amino-5-hydroxyphenyl thiocyanate, $C_7H_6ON_2S,H_2SO_4,H_2O$, probably through the intermediate formation of a hydroxylamine derivative. 2-*Amino-5-hydroxyphenyl thiocyanate*,

$$NH_2{\cdot}C_6H_3(OH){\cdot}SCN,$$

m. p. 121°, yields an *N-acetyl* derivative, m. p. 206° (decomp.) (the *methyl* ether of which has m. p. 81°), a *diacetyl* derivative, m. p. 183°, and, after diazotisation, couples with β-naphthol to form an *azo*-compound, m. p. 130°.

p-Nitrophenyl thiocyanate is reduced to *p*-aminophenyl thiocyanate at a lead or copper cathode, but in the latter case the intermediate product, p-*thiocyanoazoxybenzene*, $ON_2(C_6H_4{\cdot}SCN)_2$, m. p. 170—171°, reddish-yellow leaflets, can be isolated.

The electrolytic reduction of 2 : 4-dinitrophenyl thiocyanate, on account of its slight solubility and the consequent large volume of solution, must be effected with large stationary cathodes of lead or copper foil; also the solution (in alcoholic sulphuric acid) must be hot, and a large current density, 0·033—0·038 ampere per sq. cm., must be

employed. With a lead cathode, the product is 1 : 4-*diamino-5-hydroxybenzthiazole sulphate*, $NH_2\cdot C_6H_2(OH)<^{S}_{N}>C\cdot NH_2,H_2SO_4$, the formation of which is readily explicable in view of the course of the reduction of the *o*- and *p*-nitrophenyl thiocyanates. In favour of this constitution is the fact that the sulphate yields a *diacetylamino*-derivative, m. p. 268°, which is soluble in sodium hydroxide, and forms 1-*amino-4-acetylamino-5-methoxybenzthiazole*, m. p. 257—258°, with methyl sulphate and sodium hydroxide. When reduced at a copper cathode and with a current density of 0·05—0·06 ampere per sq. cm., 2 : 4-dinitrophenyl thiocyanate yields, at first the *sulphate* of 4-*nitro-2-amino-5-hydroxyphenyl thiocyanate*, $3C_7H_5O_3N_3S,H_2SO_4$ (*diacetyl* derivative, $C_{11}H_9O_5N_3S$, yellow, microcrystalline powder), and finally the *sulphate* of 2 : 4-*diamino-5-hydroxyphenyl thiocyanate*,

$$C_7H_7ON_3S,H_2SO_4,H_2O$$

(NN-*diacetyl* derivative, m. p. 217°; *triacetyl* derivative, m. p. 156°).

C. S.

New Halogen Compounds of the Normal Butane Series. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1911, **44**, 3699—3706. Compare Braun, Abstr., 1911, i, 610).—Phenoxybutylene, $C_4H_7\cdot OPh$, obtained on decomposition of phenoxybutyltrimethylammonium hydroxide, $OPh\cdot[CH_2]_4\cdot NMe_3\cdot OH$, yields with bromine *phenyl-γδ-dibromobutyl ether*, $OPh\cdot C_4H_7Br_2$, which is converted by hydrogen bromide into *αβδ-tribromobutane*, $CH_2Br\cdot CH_2\cdot CHBr\cdot CH_2Br$. Magnesium removes two atoms of bromine, forming *magnesium butylene bromide*, $MgBr\cdot[CH_2]_2\cdot CH:CH_2$, and this is readily converted into Δγ-pentenoic acid, $CH_2:CH\cdot CH_2\cdot CH_2\cdot CO_2H$, confirming the structural formula assigned to the preceding compounds.

Phenoxybutylene unites with hydrogen bromide to form *phenyl γ-bromobutyl ether*, $OPh\cdot[CH_2]_2\cdot CHMeBr$.

Phenoxybutylene is an oil, b. p. 208—210°/760 mm., 94—95°/16 mm.

Phenyl γδ-dibromobutyl ether is a colourless, odourless oil, b. p. 191—194°/13 mm.

αβδ-Tribromobutane is a colourless liquid of pleasant odour, b. p. 115—117°/10 mm.

The magnesium compound interacts with a variety of substances, so introducing the homoallyl complex, $CH_2:CH\cdot CH_2\cdot CH_2$; thus with benzaldehyde, *phenylbutenylcarbinol*, $OH\cdot CHPh\cdot[CH_2]_2\cdot CH:CH_2$, is obtained as a viscid, colourless liquid of ethereal odour, b. p. 125°/11 mm.

Phenyl-γ-bromobutyl ether is a colourless, odourless oil, b. p. 130—131°/9 mm. After prolonged boiling with potassium cyanide, the *nitrile* is obtained as a colourless, odourless oil, b. p. 156—157°/10 mm., and this, when boiled for ten hours with alcoholic potassium hydroxide, gives *γ-phenoxy-α-methylbutyric acid*,

$$OPh\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H,$$

which separates in lustrous, colourless crystals, m. p. 79°. The *silver* salt is a colourless, caseous precipitate.

E. F. A.

Simple Method of Formation of Hydroxyhydrindones. KARL AUWERS (*Ber.*, 1911, 44, 3692—3699. Compare Abstr., 1910, i, 629).—On heating *p*-tolyl α-bromopropionate with aluminium chloride, 7-hydroxy-4-methyl-1-hydrindone, $OH\cdot C_6H_2Me<^{CH_2}_{CO}>CH_2$, is obtained instead of *o*-bromopropionyl-*p*-cresol as expected. The structure of the hydrindone is established by the facts that it yields a semicarbazone and phenylhydrazone both soluble in alkali, and containing therefore a phenolic hydroxyl. The nucleus can be benzoylated and methylated, and this methyl derivative still forms a semicarbazone.

In a similar manner, the homologous isomeric methyl derivatives have been obtained from the *p*-tolyl α-bromobutyrate and α-bromo*iso*butyrate. It is characteristic of these oxyhydrindones that their aqueous or alcoholic solutions are coloured deep blue by ferric chloride.

It is probable in the above reaction that *p*-cresol vinyl ketone, $OH\cdot C_6H_3Me\cdot CO\cdot CH{:}CH_2$, is formed as an intermediate product. The yield of hydroxyhydrindones is only about 50% of the possible; coumaranone derivatives are also formed.

p-*Tolyl α-bromopropionate* forms colourless, lustrous needles, m. p. 33°, b. p. 145—150°/18 mm.

7-*Hydroxy*-4-*methyl*-1-*hydrindone* separates in flat, colourless, lustrous needles, m. p. 110—111°. The *semicarbazone* crystallises in colourless needles, m. p. above 280°; the *phenylhydrazone* forms lustrous, almost colourless, fatty needles, m. p. 183°. The *benzylidene* compound crystallises in faintly yellow-coloured needles, m. p. 129°. The *benzoate* is characterised by short, colourless, lustrous, fatty needles, m. p. 124—125°, and the *methyl ether* by stellate aggregates of slender, colourless, lustrous needles, m. p. 112—113°. This methyl ether forms a *semicarbazone*, colourless needles, m. p. 220—224°, and a *benzylidene* derivative, colourless, lustrous needles, m. p. 185—186°.

p-*Tolyl α-bromo*iso*butyrate* forms slender, colourless needles, m. p. 39—40°, b. p. 152°/18 mm.

7-*Hydroxy*-2 : 4-*dimethyl*-1-*hydrindone*, $OH\cdot C_6H_2Me<^{CH_2}_{CO}>CHMe$, crystallises in colourless needles, m. p. 53°; the *benzoyl* derivative yields lustrous, colourless needles, m. p. 113—114°; the *semicarbazone* gives colourless, glass-like crystals, which gradually become citron-yellow on exposure; they become brown at 220°, m. p. 230—232°.

This hydrindone does not form a benzylidene compound.

7-*Hydroxy*-3 : 4-*dimethyl*-1-*hydrindone*, $OH\cdot C_6H_2Me<^{CHMe}_{CO}>CH_2$, separates in stunted, colourless, lustrous crystals, m. p. 53—54°. The *semicarbazone* forms stunted crystals, m. p. 217°; the *benzylidene* compound gives glass-like, yellow, flat needles, m. p. 114°.

p-*Tolyl α-bromobutyrate* is an oil, b. p. 160—163°/20 mm.

E. F. A.

Retene. II. ALFRED HEIDUSCHKA and H. GRIMM (*Arch. Pharm.*, 1912, 250, 33—45. Compare Abstr., 1910, i, 397).—Retenequinone reacts with organomagnesium haloids to form dihydroxydialkyl-

dihydroretenes, and these were isolated in a crystalline condition in the case of the phenyl, benzyl, *p*-tolyl, naphthyl, and methyl derivatives, but could not be obtained pure in the case of *o*-tolyl, *m*-xylyl, bromocamphor, ethyl, or *i*-amyl derivatives. Experiments on the reduction and dehydration of dihydroxydiphenyldihydroretene are also recorded.

Dihydroxydiphenyldihydroretene, $C_{30}H_{28}O_2$, m. p. 172°, obtained by condensing magnesium phenyl bromide with retenequinone in ether, forms colourless crystals, and is coloured red by sulphuric acid, yellow by fuming nitric acid. Heated with acetyl chloride, it yields the corresponding *anhydride*, $C_{16}H_{16}<\begin{matrix}CPh\\|\\CPh\end{matrix}>O$, m. p. 143—144°, crystallising in clusters of needles, and giving when heated with potassium hydroxide in alcohol, in closed vessels, an *acid*, which probably corresponds with the product described by Acree (Abstr., 1905, i, 216) as obtained from diphenylphenanthrone; its ethereal solution is coloured blue by ammoniacal copper oxide, and then yields a *copper* derivative, $(C_{30}H_{27}O_2)_2Cu$, m. p. 142°, which at 125—140° slowly loses ammonia and turns green.

When heated with zinc dust, dihydroxydiphenyldihydroretene yields *diphenylretene*, m. p. 200°, crystallising in colourless needles from alcohol or acetone. Reduction with hydriodic acid and phosphorus gives rise to *diphenylhexahydroretene* (which forms colourless crystals, sinters at 82°, and melts completely at 118°), and eventually to Liebermann and Spiegel's retenedodecahydride.

On bromination in carbon disulphide, dihydroxydiphenyldihydroretene gives a pale yellow, finely granular powder, which on distillation with zinc yielded diphenylretene. Chlorination produced a similar product, containing 39·5% chlorine.

Dihydroxydi-p-*tolyldihydroretene*, m. p. 203°, obtained in a manner analogous to that described for the phenyl derivative, forms glancing, colourless leaflets. The *anhydride*, m. p. 152—154°, occurs in colourless, transparent, small tablets. The products of bromination and chlorination resemble those of the lower homologue. *Dihydroxydibenzyldihydroretene*, m. p. 200—201°, forms stellate clusters of small, glancing needles. *Dihydroxydinaphthyldihydroretene*, m. p. 217—218°, was isolated with some difficulty by treating the crude product with warm toluene; it yields an *anhydride*, m. p. 188°, which forms small glancing crystals from acetone or alcohol. *Dihydroxydimethyldihydroretene*, m. p. 166—167°, was eventually obtained in poor yield as small, colourless crystals, giving a violet-brown coloration with sulphuric acid.

On chlorination in carbon tetrachloride with iodine as carrier, retene furnishes a viscid product, which on precipitation from alcohol with water forms an amorphous, colourless *substance*, $C_{18}H_{14}Cl_9$ [?], m. p. 98—100°. T. A. H.

Influence of Sulphur and Sulphur-containing Groups on the Order of Substitution of Hydrogen Atoms in Benzene by Bromine. EDOUARD BOURGEOIS and A. ABRAHAM (*Rec. trav. chim.*, 1911, 30, 407—425. Compare Abstr., 1904, i, 28).—Substances

containing either of the groups $-SH$, $>S:O$, $-SO_2H$, are completely transformed by bromine. The authors have studied the action of bromine on aromatic sulphides and disulphides, sulphones and sulphonic acids. With bromine, the sulphides give rise to dibromides of the type $SRR':Br_2$, which show no tendency to split up into the sulphide and free bromine, but readily become transformed into substitution products.

Phenylmethylsulphonium dibromide, $SMePhBr_2$, is obtained as a red, crystalline substance, m. p. 87—88°, when bromine acts on phenyl methyl sulphide in carbon tetrachloride solution below 0°. Above this temperature it gives off hydrogen bromide, and is transformed into p-*bromophenyl methyl sulphide*, m. p. 37—37·5°. This, when oxidised by potassium permanganate in acetic acid solution, yields the corresponding *sulphone*, m. p. 102·5—103°, which with phosphorus pentachloride gives *p*-chlorobromobenzene. The sulphide can also be obtained by the action of methyl iodide on the sodium salt of *p*-bromothiophenol.

Diphenylsulphonium dibromide, SPh_2Br_2, is obtained by a similar reaction to the above as a red, crystalline precipitate, which still more readily passes into the corresponding *p*-bromophenyl sulphide.

Phenyl disulphide when dissolved in bromine yields *p*-dibromophenyl disulphide (compare Hübner and Alsberg, *Annalen*, 1870, **156**, 328).

Phenyl methyl sulphone is not attacked by bromine unless a catalyst, such as ferric chloride, is employed, in which case there is produced p-*bromophenylmethylsulphone*, identical with that obtained by the oxidation of the corresponding sulphide with potassium permanganate (*loc. cit.*).

In all the above cases, the bromine atom enters the para-position to the sulphur-containing group, whilst, in the case of the sulphonic acids, the group $-SO_3H$ directs the bromine to the meta-position.

W. G.

Oxonium Compounds. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1244—1257).—According to Nef's theory, the first stage of the interaction of an alkyl halide with alcoholic alkali hydroxide consists of the dissociation of the alkyl halide into halogen hydracid, which is neutralised by the alkali, and the methylene residue $R·CH:$, which either combines with the alcohol, forming a simple ether, or undergoes isomeric change into an olefine. The fact that *tert.*-butyl iodide, which is incapable of methylene dissociation, gives no ether when treated with alcoholic alkali hydroxide, is regarded as confirmation of Nef's theory. The author finds that this evidence is fallacious, since tertiary alkyl halides, such as *tert.*-amyl bromide, do give ethers under the above conditions, although the yield is very small; also *tert.*-butyl iodide yields an appreciable amount of ether if treated with the alcoholic alkali in a sealed tube. Another observation which is not in agreement with Nef's theory is that triphenylmethyl chloride reacts with alcohols, giving ethers in theoretical yields.

The most obvious method of explaining these reactions is to assume that the alkyl halogen compound, RX, dissociates into alkyl

and halogen, which then combine with the alcohol, forming an oxonium compound, $R'H\colon O\colon RX$. The latter may then decompose in two ways, giving (1) $R'\cdot O\cdot R + HX$ or (2) $R'H\colon O\colon HX$ + an olefine. These reactions would hence be closely analogous to those between alkyl halides and amines (see this vol., i, 116).

Owing to the doubt which exists concerning the intermediate formation of oxonium compounds in such reactions as the above and in the Grignard reaction, the author has studied the following reactions.

(1) The action of propyl iodide on triphenylmethyl ethyl ether in presence of magnesium. Here the first stage of the reaction consists in the formation of the oxonium compound, $CPh_3\cdot OEt\colon PrI$, which then decomposes, giving triphenylmethyl iodide and ethyl propyl ether.

(2) With the same ether as in (1), *iso*butyl iodide in presence of magnesium combines to form an oxonium derivative, which is subsequently resolved into triphenylmethyl iodide and ethyl *iso*butyl ether.

(3) Diphenylmethyl propyl ether and *iso*butyl iodide react in presence of magnesium, giving the oxonium compound,

$$CHPh_2\cdot OPrI\cdot C_4H_9,$$

which decomposes in three ways, giving (*a*) $CHPh_2I + C_4H_9\cdot OPr$; (*b*) $C_4H_9I + CHPh_2\cdot OPr$; and (*c*) $C_3H_7I + CHPh_2\cdot O\cdot C_4H_9$(?).

Diphenylmethyl propyl ether, $CHPh_2\cdot OPr$, prepared by the interaction of diphenylbromomethane and propyl alcohol in presence of potassium hydroxide, is a colourless, mobile liquid, b. p. 161°/11 mm.

T. H. P.

Some Chlorine Derivatives of Cholesterol. STEPHAN MINOVICI and BELLA HAUSKNECHT (*Biochem. Zeitsch.*, 1912, 38, 46—52).—When cholesterol in alcoholic solution is treated with chlorine gas, two substances are formed; one, $C_{40}H_{72}O_3Cl_2$ or $C_{42}H_{72}O_3Cl_2$, is soluble in alcohol and contains water of crystallisation, m. p. 125°, and when anhydrous, m. p. 130°; the other, $C_{56}H_{104}O_5Cl_2$, m. p. 195° (precipitated from ethereal solution by alcohol), is insoluble in alcohol. The formation of the former substance can be explained on the assumption that two molecules of cholesterol combine to form an ether, from which by the chlorinating and oxidising action of the chlorine, two vinyl and two *iso*butyl groups are eliminated and replaced by hydroxyl and chlorine. By the action of hydrogen chloride and hydrogen peroxide, a third chlorine derivative, $C_{26}H_{47}OCl$, was obtained; it forms slender needles containing water of crystallisation, m. p. 123°.

S. B. S.

Preparation of Arylpolymethylenechloro-compounds. EMANUEL MERCK (D.R.-P. 238959).—When benzo-ε-chloroamylamide, $C_6H_5\cdot CO\cdot NH\cdot[CH_2]_5Cl$ is heated with aluminium chloride in benzene solution and the mixture subsequently treated with steam, it yields *benzo-ε-phenylamylamide*, $C_6H_5\cdot CO\cdot NH\cdot[CH_2]_5\cdot Ph$, a yellow oil, b. p. 273—275°/15 mm., which on hydrolysis furnishes *ε-phenylamyl-*

amine, $NH_2\cdot[CH_2]_5Ph$, b. p. 131°/15 mm., *picrate*, m. p. 152—153°, and *platinichloride*, m. p. 220°.

ε-Chloroamylbenzene, obtained by heating the foregoing benzophenylamylamide with phosphorus pentachloride, has an unpleasant odour and b. p. 134°/18 mm.

Benzo-δ-phenylbutylamide, glistening needles, m. p. 83·5°, is analogously prepared from benzochlorobutylamide with phosphorus pentachloride; it furnishes *δ-chlorobutylbenzene*, $C_6H_5\cdot[CH_2]_4Cl$, b. p. 122—123°/17 mm.

F. M. G. M.

Preparation of Derivatives of *o*-Thiolbenzoic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 237773).—When dichloroethylene (1 mol.) reacts with an alcoholic solution of a thiolbenzoic acid (2 mols.), it yields acetyl*bis*thiolbenzoic acids (*bis*methinethiolbenzoic acids) of the general formula $CO_2R'\cdot R\cdot S\cdot CH\colon CH\colon S\cdot R\cdot CO_2R'$, where R is a benzene or naphthalene residue, and R′ a metal, aryl, or alkyl group. The preparation of acetylene*bis*thiolbenzoic acid is described.

F. M. G. M.

Products Formed by the Action of Heat on *p*-Sulphamidobenzoic Acid. W. B. STODDARD (*Amer. Chem. J.*, 1912, 47, 1—20).—Remsen and Muckenfuss (Abstr., 1896, i, 481) found that when *p*-sulphamidobenzoic acid is heated at 220° for eight hours, there are formed *p*-sulphobenzoic acid, ammonium hydrogen *p*-sulphobenzoate, an "infusible diamide of *p*-sulphobenzoic acid," and "*iso-p*-sulphamidobenzoic acid."

When the "infusible diamide" is heated with phosphorus pentachloride at 194—197°, *p*-chlorobenzonitrile is produced. An attempt was made to remove one of the nitrogen atoms, whilst leaving the other, by heating the compound with hydrochloric acid, but without success. It was also found that the desired result could not be attained by diazotisation or by heating with sodium carbonate solution. When a current of steam was passed through a mixture of the diamide and magnesium hydroxide, ammonia was liberated, and a *magnesium* salt was obtained of an acid, isomeric with *p*-sulphamidobenzoic acid, but entirely different from "*iso-p*-sulphamidobenzoic acid." The corresponding *potassium* salt reacts readily with phosphorus pentachloride, but the infusible diamide is not thereby regenerated. These facts indicate that the nitrogen atoms of the infusible diamide are both attached to carbon, and that the acid isomeric with *p*-sulphamidobenzoic acid is probably *p*-carbamidobenzenesulphonic acid.

When Remsen and Muckenfuss' "*iso-p*-sulphamidobenzoic acid" is heated in a sealed tube with concentrated hydrochloric acid at 100°, the infusible diamide is produced. If the acid is heated in a sealed tube with water at 220°, a small quantity of a substance is produced which crystallises in thin plates. Analyses of the barium and sodium salts of "*iso-p*-sulphamidobenzoic acid" have shown that this acid is not isomeric with *p*-sulphamidobenzoic acid, but has the composition of an anhydride of the latter, $C_6H_4{<}{}^{CO-}_{SO_2}{>}NH$. Determinations have

been made of the electrical conductivity of solutions of both these acids.

It is suggested that the action of heat on *p*-sulphamidobenzoic acid may be represented by the equation:

$$4CO_2H\cdot C_6H_4\cdot SO_2\cdot NH_2 = C_6H_4<^{CO-}_{SO_2}>(NH_2)_2 + CO_2H\cdot C_6H_4\cdot SO_3H +$$
$$CO_2H\cdot C_6H_4\cdot SO_2\cdot ONH_4 + C_6H_4<^{CO}_{SO_2}>NH.$$

E. G.

Bornylene from β-Iodohydrobornylenecarboxylic [β-Iodocamphanecarboxylic] Acid: Dibromobornylenecarboxylic [αβ-Dibromocamphanecarboxylic] Acid and Dihydrobornylenecarboxylic [*ortho*-Camphanecarboxylic] Acid. JULIUS BREDT and W. HILBING (*J. pr. Chem.*, 1911, [ii], 84, 778—786. Compare Abstr., 1910, i, 498).—*β-Iodocamphanecarboxylic acid*,

$$C_8H_{14}<^{CH\cdot CO_2H}_{CHI},$$

prepared by the action of hydrogen iodide on a glacial acetic acid solution of bornylenecarboxylic acid, crystallises in needles, m. p. 129—130°. It dissolves in hot aqueous sodium carbonate, yielding a crystalline *sodium* salt, together with the hydroxy-acid, $C_{11}H_{18}O_3$, previously described (*loc. cit.*). When heated with strong aqueous sodium hydroxide, the sodium salt yields bornylene, which has $[\alpha]_D^{20} - 23{\cdot}68°$ in toluene, and $[\alpha]_D^{19} - 23{\cdot}94°$ in benzene. A glacial acetic acid solution of bornylene, when heated at 70° with sulphuric acid, yields a bornyl acetate, b. p. 103—104°/14 mm., which, on hydrolysis, furnishes a borneol of m. p. 175—178°.

αβ-Dibromocamphanecarboxylic acid, $C_8H_{14}<^{CBr\cdot CO_2H}_{CHBr}$, obtained by the addition of bromine to bornylenecarboxylic acid in carbon tetrachloride solution, and purified by means of the *sodium* salt, crystallises in needles, m. p. 159—160°.

ortho-Camphanecarboxylic acid (*loc. cit.*), prepared by reducing β-iodocamphanecarboxylic acid, yields a *chloride*, b. p. 114—115°/14 mm., and an *amide*, m. p. 166—167°, which is converted by the Hofmann reaction into an *amine* of the annexed formula. Improvements in the preparation of bornylenecarboxylic acid are also described.

$$\begin{array}{l} CH_2\cdot CH—CH\cdot NH_2 \\ \quad\;\; | \quad CMe_2 \quad | \\ CH_2\cdot CMe\cdot CH_2 \end{array}$$

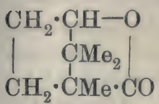
Ethyl bornylenecarboxylate, obtained as a by-product in crystallising the anhydride from alcohol, has b. p. 121—122°/16 mm.

F. B.

Electrolytic Reduction of Camphononic Acid to *cis-trans*-Camphonolic Acid: Camphonololactone. JULIUS BREDT [and, in part, with WILHELM LUND and AUGUST AMANN] (*J. pr. Chem.*, 1911, [ii], 84, 786—799).—When subjected to electrolytic reduction, camphononic acid yields a mixture of two stereoisomeric camphonolic acids,

$$\begin{array}{l} OH\cdot CH\cdot CMe_2 \\ \;\;\;\;\;\;\; | \\ \;\;\;\;\;\; CH_2-CH_2 \end{array}\!\!>CMe\cdot CO_2H,$$

which may be separated by distillation, whereby the *cis*-camphonolic acid is converted into the corresponding lactone, whilst the *cis-trans*-isomeride distils unchanged.



cis-*Camphonololactone* (annexed formula) has m. p. 160—161°, b. p. 239·2°, $[\alpha]_D^{17}$ − 16·2° in alcohol.

cis-*Camphonolic acid* is obtained by the addition of the calculated amount of cold dilute hydrochloric acid to its *barium* salt, which is prepared by the action of barium hydroxide on the preceding lactone. It has $[\alpha]_D^{20}$ − 33·4° in alcohol, and a varying m. p. according to the rapidity of heating; when rapidly heated, it has m. p. 197—198°.

The isomeric cis-trans-*camphonolic acid* has m. p. 249—250°.

γ-*Bromocamphonanic acid*, $\begin{array}{l}CHBr\cdot CMe_2\\ CH_2{-}{-}{-}CH_2\end{array}\!\!>CMe\cdot CO_2H$, obtained by the action of saturated aqueous hydrobromic acid on the *cis*-lactone, has m. p. 146—147°, and when treated with aqueous sodium carbonate is reconverted into the lactone.

Both *cis-trans*-camphononic acid and *cis*-camphonololactone are oxidised by concentrated nitric acid to camphoronic acid.

Improvements in the method of preparing camphononic acid (Lapworth and Lenton, Trans., 1901, 79, 1287) are also described.

F. B.

Resolution of Mandelic Acid into its Active Components by means of Phenylethylamine. LENNART SMITH (*J. pr. Chem.*, 1911, [ii], 84, 743—744).—The resolution of *r*-mandelic acid has been accomplished by crystallising the *l*-β-phenylethylamine salt from water, the salt of the *d*-acid being the less soluble. The pure *d*-acid is obtained from the mandelic acid, recovered from the mother liquor, by crystallisation with *d*-phenylethylamine. F. B.

Atrolactic [α-Hydroxy-α-phenylpropionic] Acid. LENNART SMITH (*J. pr. Chem.*, 1911, [ii], 84, 731—743).—The first part of this paper contains an account of a large number of experiments on the formation of acetophenonecyanohydrin, and the hydrolysis of the latter compound to atrolactic acid. This is followed by a description of the resolution of the acid into its optically active components, and of its behaviour towards hydrochloric acid.

In the preparation of atrolactic acid by Spiegel's method (Abstr., 1881, 277; compare Staudinger and Ruzicka, Abstr., 1911, i, 462), better yields are obtained by replacing the hydrochloric acid by glacial acetic acid.

Atrolactic [α-hydroxy-α-phenylpropionic] acid crystallises with $\frac{1}{2}H_2O$, and the *potassium*, *sodium*, and *magnesium* salts with $2H_2O$; the *strontium* salt, $Sr(C_9H_9O_3)_2,4H_2O$, and *calcium* salt, $CaH_2(C_9H_9O_3)_4$, m. p. 216° (decomp.), are also described; the affinity constant $K = 0\cdot0341$.

The resolution of the acid into its optically active component is accomplished by crystallisation of its salt with *l*-β-phenylethylamine, the salt of the *d*-acid being the less soluble (compare McKenzie and Clough,

Trans., 1910, 97, 1016). The pure *l*-acid is obtained by crystallising the acid recovered from the mother liquors with *d*-phenylethylamine. The l-*phenylethylamine* salts of both the *d*- and the *l*-acids were analysed. The *barium*, $BaX_2,\frac{1}{2}H_2O$, *calcium*, $CaX_2,3\frac{1}{2}H_2O$, and *potassium*, $KX,2H_2O$, salts of the active acids are also described ($X = C_9H_9O_3$).

Hydratropic acid is readily obtained from atrolactic acid by heating it with concentrated hydrochloric acid for three-quarters of an hour on the water-bath, and reducing the product with sodium amalgam. When heated with concentrated hydrochloric acid for four hours at 130—135°, atrolactic acid yields β-chloro-α-phenylpropionic acid together with α- and β-*iso*atropic acids. By heating tropic acid at 170—180°, it is converted into atropic acid, which is accompanied by small quantities of α- and β-*iso*atropic acids.

From these experiments the conclusion is drawn that the action of hydrochloric acid on atrolactic acid yields successively atropic, β-chloro-α-phenylpropionic, and *iso*atropic acids. F. B.

α-Phenyl-α-ethylglycollic Acid. Lennart Smith (*J. pr. Chem.* 1911, [ii], **84**, 744—745).—α-Phenyl-α-ethylglycollic [α-hydroxy-α-phenylbutyric] acid is best prepared by the addition of glacial acetic acid to a mixture of potassium cyanide and propiophenone, and hydrolysis of the nitrile thus obtained by means of hydrogen chloride in ethereal solution, the resulting amide being finally hydrolysed by aqueous sodium hydroxide. It crystallises in needles, m. p. 132° (corr.) (compare Grignard, Abstr., 1903, i, 32), and is resolved into its optically active components by crystallisation of the *d*-β-phenylethylamine salt. *l-α-Hydroxy-α-phenylbutyric acid* has, in aqueous solution, $[\alpha]_D^{18} - 14°$. F. B.

Ethyl Anisoylacetates. André Wahl and C. Silberzweig (*Bull. Soc. chim.*, 1912, [iv], **11**, 25—34. Compare Abstr., 1908, i, 647; 1910, i, 263).—Ethyl *m*- and *p*-methoxybenzoylacetates have been prepared by condensing ethyl acetate with ethyl *m*- and *p*-methoxybenzoates in presence of sodium. The corresponding *ortho*-compound has already been prepared by Tahara (Abstr., 1892, 844).

Ethyl p-*anisoylacetate*, $OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO_2Et$, is a pale yellow liquid, b. p. 180—190°/10—12 mm., decomposing partly into *p*-anisoyldehydracetic acid. It yields a green *copper* salt, $(C_{12}H_{13}O_4)_2Cu$, m. p. 210°, and a *nitroso*-derivative, m. p. 113—114°.

Ethyl m-*methoxybenzoylacetate* also decomposes very readily on distillation. It yields a green *copper* salt, m. p. 168—169°, and a *nitroso*-derivative, m. p. 94°. W. G.

Preparation of Halogenated 2-Anthraquinonylaminobenzoic Acids. Fritz Ullmann (D.R.-P. 238106. Compare Abstr., 1906, i, 426, 953; 1910, i, 270).—4-*Bromo-2-anthraquinonylaminobenzoic acid*, $C_{14}H_7O_2\cdot NH\cdot C_6H_3Br\cdot CO_2H$, a violet powder, which does not fuse at 300°, is obtained by heating 1-chloroanthraquinone (24·2 parts) with 4-bromoanthranilic acid (22 parts), potassium acetate (20 parts), copper acetate (1 part), and copper powder (1 part) at 160° in amyl-alcoholic solution. F. M. G. M.

Fagaramide, a New Nitrogenous Substance from the Root-bark of Fagara xanthoxyloides. HERMANN THOMS and F. THÜMEN (*Ber.*, 1911, **44**, 3717—3730).—The root-bark of *Fagara xanthoxyloides* contains a nitrogenous substance, $C_{14}H_{17}O_3N$, crystallising from alcohol in well-formed crystals, m. p. 119—120°. Thirty grams were obtained from 40 kilos. of the drug. The compound termed *fagaramide* is identified as the iso*butylamide* of *piperonylacrylic acid*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CHMe_2.$$

On prolonged boiling with 50% alcoholic potassium hydroxide, it is decomposed into *iso*butylamine and piperonylacrylic acid.

Fagaramide is prepared synthetically by condensing piperonylacrylic chloride and *iso*butylamine in ethereal solution. In a similar manner, the isomerides are prepared, namely, the normal, secondary, and tertiary butylamides of piperonylacrylic acid. All four isomerides form characteristic, crystalline dibromo-derivatives.

Fagaramide reacts neutral, and does not form salts; it belongs to the same group as piperine.

All four isomerides have the same physiological action, namely, narcotic on cold-blooded animals, but practically none on warm-blooded animals.

Fagaramide is obtained by extraction with benzene. The *dibromide*, $C_{14}H_{17}O_3NBr_2$, forms slender, colourless needles, m. p. 154—155°.

On oxidation of fagaramide, piperonal and piperonylic acid, m. p. 230° (not 227·5—228°), are obtained. Piperonylacrylic acid has m. p. 242° (not 238° or 232—234° as stated in the literature). *iso*Butylamine hydrochloride has m. p. 177—178° (not 160°).

Piperonylacrylic chloride, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}COCl$, is conveniently prepared by the action of thionyl chloride on the acid.

Piperonylacryl-n-*butylamide*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}NH{\cdot}[CH_2]_3{\cdot}CH_3,$$

forms very minute crystals, m. p. 85—86°. The *dibromide* separates in small, colourless needles, m. p. 134—135° (decomp.).

Piperonylacryl-sec.-*butylamide*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}NH{\cdot}CHMeEt,$$

yields colourless needles, m. p. 161—162°; the *dibromide* has m. p. 164—165° (decomp.).

Piperonylacryl-tert.-*butylamide*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}NH{\cdot}CMe_3$, forms strongly refractive, pale yellow prisms, which are colourless when powdered, m. p. 138—139°; the *dibromide* crystallises in slender, colourless needles, m. p. 182—183° (decomp.). E. F. A.

Aminosulphones and Allied Compounds. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1911, **44**, 3628—3636).—The analogous behaviour of ketones and sulphones in many reactions led the authors to hope that γ- and δ-aminosulphones might yield heterocyclic bases, just as γ- and δ-amino-ketones yield pyrrolines and tetrahydropyridines respectively. This expectation has not been fulfilled, but the work has led to the production of the following substances.

When warmed with phosphorus pentachloride, phthalyltaurine yields *phthalyltauryl chloride*, $C_6H_4{<}^{CO}_{CO}{>}N{\cdot}C_2H_4{\cdot}SO_2Cl$, m. p. 160°.

This substance is very stable to hot water, does not react with benzene and aluminium chloride, but is converted into the *methyl* ester,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_2H_4\cdot SO_3Me,$$

m. p. 103—104°, by methyl-alcoholic sodium methoxide.

Phenyl β-phthalimidoethyl sulphone,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CH_2\cdot SO_2Ph,$$

m. p. 185—185·5°, obtained from benzenesulphinic acid, alcoholic sodium ethoxide, and β-bromoethylphthalimide at 100°, yields, by hydrolysis by acetic acid and hydrochloric acids at 140°, *phenyl-β-aminoethylsulphone hydrochloride*, $NH_2\cdot CH_2\cdot CH_2\cdot SO_2Ph,HCl$, m. p. 155—155·5°, glistening needles. *Phenyl-γ-phthalimidopropylsulphone*, m. p. 126°, and *phenyl-γ-aminopropylsulphone hydrochloride*, m. p. 222°, are obtained by similar methods from γ-iodopropylphthalimide. Phenyl mercaptan and β-bromoethylphthalimide react with boiling alcoholic potassium hydroxide to form *phenyl β-phthalimidoethyl sulphide*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CH_2\cdot SPh$, m. p. 59—60°, long needles, by the hydrolysis of which *phenyl β-aminoethyl sulphide hydrochloride*, $NH_2\cdot CH_2\cdot CH_2\cdot SPh,HCl$, m. p. 160—161°, is obtained.

β-Phthalimidoethyl mercaptan is converted by warm nitric acid, D 1·2, into *β-phthalimidoethyldisulphoxide*,

$$\left(C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CH_2\right)_2S_2O_2,$$

m. p. 155—156°, which reacts in benzene with aluminium chloride on the water-bath to form, after treating the product with hydrochloric acid, *β-phthalimidoethylsulphinic acid*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CH_2\cdot SO_2H,$$

m. p. 149—149·5° (decomp.), glistening, white leaflets. This acid, which is also obtained by reducing the disulphoxide or phthalyltauryl chloride by zinc dust and 96% alcohol, is decomposed by boiling 20% hydrochloric acid, yielding phthalic acid, taurine, and β-phthalimidoethyldisulphoxide. C. S.

Action of α-Hydroxy*iso*butyronitrile on the Nitrile Ester of Iminodi-phenylacetic Acid. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1235—1244).—It has been previously suggested (Abstr., 1909, i, 771, 772; 1910, i, 825) by the author that in the action of α-hydroxypropionitrile on the nitrile esters of propionyliminocycloheptanecarboxylic and iminodi-phenylacetic acids, an intermediate, unstable compound of the ammonium hydroxide type is formed, this then undergoing decomposition into other hydroxy-nitriles and nitrile esters of imino-acids. Such intermediate formation of ammonium hydroxide compounds is assumed also (1) in the formation of amines and amino-, imino-, and nitrilo-acids by the action of hydroxy-nitriles on either ammonia or its derivatives; (2) in the interaction of alkyl halides or halogen derivatives of acids with ammonia or its organic derivatives, and in a number of other reactions.

Most of the reactions represented in this way are explained equally well by Nef's "methylene-dissociation"; thus the interaction of the nitrile ester of iminodi-phenylacetic acid and α-hydroxypropionitrile may be regarded as occurring in the following stages: (1) the hydroxynitrile dissociates into methylene derivative and water: $CH_3{\cdot}CH(OH){\cdot}CN = CH_3{\cdot}C(CN){:} + H_2O$; (2) water and the nitrile ester give the ammonium hydroxide compound,

$$CN{\cdot}CHPh{\cdot}NH_2(OH){\cdot}CHPh{\cdot}CO_2Et;$$

(3) the ethylidenecyanogen combines with the ammonium hydroxide compound, giving the nitrile ester of a nitrilo-acid,

$$CN{\cdot}CHPh{\cdot}NH(OH)(CHMe{\cdot}CN){\cdot}CHPh{\cdot}CO_2Et,$$

which then decomposes into derivatives of an imino-acid of lower molecular weight and mandelonitrile.

In order to arrive at a decision between these two explanations, the author has investigated the action of α-hydroxy*iso*butyronitrile, which is incapable of methylene dissociation on the nitrile ester of iminodi-phenylacetic acid. The result confirms the author's view of these reactions, the product of the reaction being anhydronitrilodi*iso*butyricphenylacetic acid,

$$CO_2H{\cdot}CHPh{\cdot}N{<}\begin{matrix}CMe_2{\cdot}CO\\CMe_2{\cdot}CO\end{matrix}{>}O,$$

which is formed as follows: $CN{\cdot}CHPh{\cdot}NH{\cdot}CHPh{\cdot}CO_2Et$ + $OH{\cdot}CMe_2{\cdot}CN$ = $CN{\cdot}CHPh{\cdot}NH(OH)(CMe_2{\cdot}CN){\cdot}CHPh{\cdot}CO_2Et$ = $OH{\cdot}CHPh{\cdot}CN$ + $CN{\cdot}CMe_2{\cdot}NH{\cdot}CHPh{\cdot}CO_2Et$; the latter + $OH{\cdot}CMe_2{\cdot}CN = CN{\cdot}CMe_2{\cdot}NH(OH)(CMe_2{\cdot}CN){\cdot}CHPh{\cdot}CO_2Et = H_2O$ + $CN{\cdot}CMe_2{\cdot}N(CMe_2{\cdot}CN){\cdot}CHPh{\cdot}CO_2Et$. This nitrile ester then undergoes hydrolysis to the substituted triacetic acid, which is subsequently transformed into the corresponding anhydride.

*Anhydronitrilodi*iso*butyricphenylacetic acid*, $C_{16}H_{19}O_5N$ (see above), crystallises from aqueous alcohol in silky needles, m. p. 180—181° (slowly heated in sealed capillary). As would be expected from the fact that iminodicarboxylic acids are rendered neutral to phenolphthalein by one equivalent of alkali hydroxide, two equivalents of the latter are sufficient to neutralise this anhydride. T. H. P.

Photochemical Behaviour of Nitroterephthalaldehyde. Hermann Suida (*J. pr. Chem.*, 1911, [ii], **84**, 827—830).—The author finds that nitroterephthalaldehyde is very sensitive to light. A cold xylene solution of the aldehyde on exposure to direct sunlight rapidly becomes turbid, and deposits a yellow solid consisting of 2-*nitroso-4-aldehydobenzoic acid*, $CHO{\cdot}C_6H_3(NO){\cdot}CO_2H$. The acid slowly chars at 250—300°, but when placed in a bath at 300° instantly melts with decomposition. It dissolves in alkalis and alkaline carbonates, yielding yellowish-green solutions. Its solution in concentrated sulphuric acid develops with a trace of phenol an emerald-green coloration.

Details of a lecture experiment illustrating the photochemical transformation of the aldehyde are given. F. B.

Angeli-Rimini Reaction of the Aldehydes. Angelo Angeli (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 445—449. Compare Balbiano, Abstr., 1911, i, 987).—The author has prepared Wallach's ketone, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}COMe$, and Balbiano's product from anethole

glycol, and finds that they are identical, and do not give the Angeli-Rimini reaction when it is carried out as originally described. The reaction, however, is given by these substances when an excess of alkali is employed. This explains Balbiano's results. It is advisable to add the calculated quantity of alkali in small portions (compare Angeli and Castellana, Abstr., 1909, i, 392), and in the qualitative test it is better to use the sodium salt of Piloty's acid. Deoxybenzoin, benzoin, benzil, and dibenzyl ketone behave similarly, giving the reaction only when an excess of alkali is employed. R. V. S.

o-Hydroxyacetophenone, 5-Chloro-o-hydroxyacetophenone, and Certain Chlorochalkones and Chloroflavones. FRANZ KUNCKELL [with ALBERT FÜRSTENBERG] (*Ber.*, 1911, 44, 3654—3656. Compare Abstr., 1901, i, 213).—The authors describe the preparation of o-hydroxyacetophenone from 5-acetylamino-2-hydroxyacetophenone, and of 5-ω-*dichloro-2-hydroxyacetophenone* (m. p. 64°) from ω-chloro-5-amino-2-hydroxyacetophenone. The corresponding *ω-chloro-5-bromo-2-hydroxyacetophenone* has m. p. 68°.

5-Chloro-2-hydroxyacetophenone condenses with benzaldehyde in the presence of sodium hydroxide to form 5-*chloro-2-hydroxychalkone*, m. p. 108°, which readily combines with bromine to form a *dibromide* of m. p. 185°. H. W.

Chalkone and Hydrochalkones. GUIDO BARGELLINI and LEDA BINI (*Gazzetta*, 1911, 41, ii, 435—445).—Hydrochalkones may be prepared conveniently by reducing chalkones with hydrogen in the presence of platinum-black. In this way, from an ethereal solution of 2-hydroxychalkone, 2-hydroxydihydrochalkone was obtained; the product is best purified by conversion into the *semicarbazone*, $C_{16}H_{17}O_2N_3$, which forms white needles, m. p. 174—175° (softening at 170°).

The reduction of 4-methoxychalkone with zinc dust and acetic acid yielded a *substance* (probably a diketonic condensation product), $C_{32}H_{30}O_4$, which crystallises in colourless needles, m. p. 224—225°. When 4-methoxychalkone in ethereal solution is reduced with hydrogen in presence of platinum-black, 4-*methoxydihydrochalkone*, $C_{16}H_{16}O_2$, is obtained; it crystallises in colourless needles, m. p. 59—60° (softening at 55°), and it gives a yellow coloration with concentrated sulphuric acid. The *semicarbazone*, $C_{17}H_{19}O_2N_3$, forms colourless needles, m. p. 118—120°.

3 : 4-Dimethyleneoxychalkone, when reduced with zinc and acetic acid, yields a *substance*, $C_{32}H_{26}O_6$, which crystallises in colourless needles, and is solid at 260°. When the reduction is effected with hydrogen in the presence of platinum-black, 3 : 4-*dimethyleneoxydihydrochalkone*, $C_{16}H_{14}O_3$, is produced; it crystallises in colourless needles, m. p. 39—40° (softening at 35°), and gives a red coloration with concentrated sulphuric acid. The *semicarbazone*, $C_{17}H_{17}O_3N_3$, forms colourless needles, m. p. 153—154°. R. V. S.

Preparation of Benzoylaminohydroxyanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 238488).—When 1 : 5-dibenzoyldiaminoanthraquinones are oxidised with either

manganese dioxide, a persulphate or a perchlorate, a hydroxy-group is introduced into either position 4 or 8.

1 : 5-Dibenzoyldiaminoanthraquinone (10 parts) dissolved in 100 parts of sulphuric acid (10% SO_3) was slowly treated at 5—10° with manganese dioxide (3·5 parts), maintained below 15° with continual stirring during two hours, and the *4-hydroxy-1 : 5-dibenzoyldiaminoanthraquinone* subsequently isolated by known methods.

4-Chloro-8-hydroxy-1 : 5-dibenzoyldiaminoanthraquinone was prepared in a similar manner with potassium persulphate from 4-chloro-1 : 5-dibenzoyldiaminoanthraquinone, whilst 2-chloro-1 : 5-dibenzoyldiaminoanthraquinone furnished *2-chloro-4(8)-hydroxy-1 : 5-dibenzoyldiaminoanthraquinone.* F. M. G. M.

Preparation of Dianthraquinonyl- or Polyanthraquinonyl carbamides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P 238550, 238551, 238552, and 238553. Compare Abstr., 1911, i, 469, 655, 995).—The preparation of dianthraquinonylcarbamides has previously been described, and the reaction has now been extended to the case of heteronuclear $\beta\beta'$-diaminoanthraquinones.

These *compounds*, orange-yellow powders, are obtained by the action of *$\beta\beta'$-anthraquinonylenedicarboxyl chlorides* (obtained from 2 : 6- or 2 : 7-diaminoanthraquinones with excess ef carbonyl chloride) on amino- or diamino-anthraquinones.

The second and third patents state that $\beta\beta'$-dianthraquinonylcarbamide can be readily prepared by heating β-aminoanthraquinone at 170° with carbamide or ethyl urethane, either with or without solvent, until evolution of ammonia (and in the latter case, alcohol) ceases. The fourth patent deals with the employment of substituted aryl- or diaryl-carbamides, and describes *p-tolyl-2-anthraquinonylcarbamide*, yellow crystals, obtained by the prolonged boiling of *p*-toluidine with 2 : 2′-dianthraquinonylcarbamide. F. M. G. M.

[Preparation of Anthracene Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 238980).—It is now found that the compounds previously described (Abstr., 1907, i, 226) can be prepared from 1 : 1′-dianthraquinonyl-2 : 2′-dialdehyde by reduction with either an alkaline solution of sodium hyposulphite or with zinc in concentrated sulphuric acid solution. F. M. G. M.

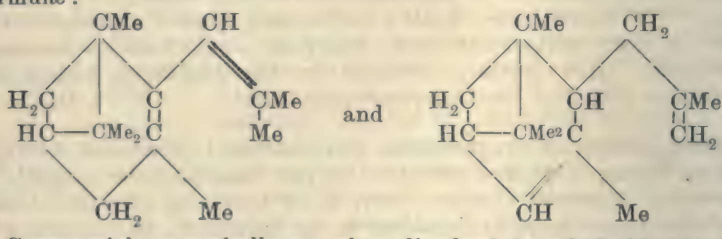
Decomposition of Alkylidenehydrazines: Conversion of Ionone and ψ-Ionone into the Corresponding Hydrocarbons, $C_{13}H_{22}$. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1398—1402).—The decomposition of iononehydrazone in presence of potassium hydroxide is an exothermic reaction, and gives rise to *a-ionane*, $CHEt:CH\cdot CH<\substack{CMe_2\cdot CH_2 \\ CMe{=}CH}>CH_2$, which is a colourless liquid with a faint odour of turpentine, b. p. 220—221°/747 mm., D_0^{20} 0·8530, n_D 1·4784. It readily oxidises in the air, combines with 4 atoms of bromine, and in acetic anhydride solution gives a raspberry-red coloration with a drop of sulphuric acid. It shows the normal molecular refraction, whereas the similar hydrocarbon corresponding

with β-ionone should exhibit considerable exaltation, owing to the presence of conjugated double bonds.

ψ-Ionane, CHEt:CH·CH$_2$·CMe:CH·CH$_2$·CH:CMe$_2$ (?), obtained in a similar manner from ψ-ionone, is a colourless, faintly-smelling liquid, b. p. 224—225°/751 mm., D_0^{20} 0·8151, n_D 1·4725; it rapidly turns yellow in contact with the air, unites with 6 atoms of bromine, and is converted into α-ionane when its acetic acid solution is boiled with a small quantity of sulphuric acid. The formula given above is of doubtful accuracy, as the hydrocarbon does not exhibit optical exaltation. T. H. P.

Crystalline Form and Optical Characters of Pinocampheol Methyl Xanthate. N. I. Surgunoff (*Zeitsch. Kryst. Min.*, 1911, **50**, 62—63; from *Bull. Soc. Nat. Moscow*, 1907, 543—551).—The crystals of pinocampheol methyl xanthate (Tschugaeff, Abstr., 1908, i. 93) are orthorhombic with $a:b:c = 1·3747:1:0·9787$. L. J. S.

Constituents of Essential Oils. The Constitution of the Active Caryophyllenes; Transformation of the Active Caryophyllenes into Monocyclic Derivatives. Friedrich W. Semmler and Erwin W. Mayer (*Ber.*, 1911, **44**, 3657—3679).—The authors have subjected caryophyllene to the action of ozone, and studied the decomposition products of the ozonide so formed. They consider that crude caryophyllene is composed chiefly of three caryophyllenes, namely, Deussen's inactive α-caryophyllene and two active caryophyllenes, which they name *terp.*-caryophyllene and *lim.*-caryophyllene, and to which they assign the respective provisional formulæ:



Commercial caryophyllene, when dissolved in ethyl chloride and subjected to the action of ozone, yields a soluble *ozonide*, $C_{15}H_{24}O_6$, together with a small quantity of an insoluble *ozonide*, which probably contains seven or eight atoms of oxygen. When the soluble ozonide is heated in glacial acetic acid solution, it yields carbon dioxide and formaldehyde, together with a mixture of acidic and neutral products. From the acidic products a keto-acid, $C_{11}H_{18}O_3$, a diketo-acid, $C_{14}H_{22}O_4$, and an acid, $C_8H_{14}O_2$, were isolated.

The *keto*-acid, $C_{11}H_{18}O_3$, is a pale yellow, mobile oil of b. p. 183—187°/11·5 mm., D^{20} 1·040, α_D^{20} +44°, n_D^{20} 1·4677. Its *silver* salt was analysed. The *methyl* ester has b. p. 139—142°/15·5 mm., D^{20} 0·9913, n_D^{20} 1·4527, α_D^{20} +42°. The *semicarbazone* has m. p. 183°. When oxidised with nitric acid, the keto-acid yields dimethylsuccinic acid and dibasic *caryophyllenic acid*, $C_9H_{14}O_4$. The latter forms a non-crystalline syrup of b. p. 215—218°/9 mm., 222—225°/13 mm. It is

remarkably stable towards nitric acid. The *silver* and *copper* salts were prepared. The *methyl* ester has b. p. 127—131°/11 mm., D^{20} 1·0456, n_D^{20} 1·4462, α_D^{20} +44°. When boiled with acetic anhydride, caryophyllenic acid yields an *anhydride* of b. p. 152—158°/10 mm., D^{20} 1·1399, n_D^{20} 1·4755, α_D^{20} −28°. Similar products were obtained when the keto-acid was oxidised by bromine in alkaline solution. Oxidation with permanganate also gave caryophyllenic acid, to which the formula $CH_2<\begin{matrix}CMe(CO_2H)\\CH(CO_2H)\end{matrix}>CMe_2$ is assigned.

The *diketo*-acid, $C_{14}H_{22}O_4$, is a viscous, yellow oil of b. p. 229—232°/11·5 mm., D^{20} 1·0830, n_D^{20} 1·4804, α_D^{20} +41°. Its *silver* salt begins to darken at 130°, and has m. p. about 145°. Its *methyl* ester has b. p. 184—188°/12 mm., D^{20} 1·047, α_D^{20} +38°, n_D 1·4680. With semicarbazide hydrochloride it gives no product of definite m. p. When oxidised with nitric acid, it yields succinic acid and caryophyllenic acid. On treatment with bromine in alkaline solution, it yields caryophyllenic acid, together with a mixture of acids of high boiling point.

The *acid*, $C_8H_{14}O_2$, has b. p. 120—128°/9 mm., D^{20} 0·9827, n_D 1·4457, $[\alpha]_D$ + 17°, and is monobasic. Its *methyl* ester has b. p. 64—68°/9 mm., D^{20} 0·922, $[\alpha]_D^{20}$ + 20°, n_D 1·4316. Its *amide* melts at 96°.

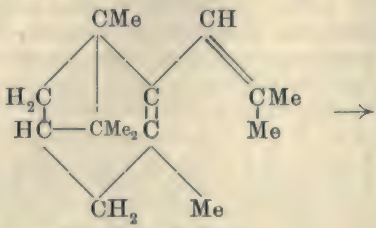
From the neutral portion (see above), a ketone, $C_{10}H_{18}O$, a probable *keto-aldehyde*, $C_{11}H_{18}O_2$, a diketone, $C_{12}H_{20}O_2$, and a deketo-aldehyde, $C_{14}H_{22}O_3$, were isolated.

The *ketone*, $C_{10}H_{18}O$, is a mobile, pale green liquid of b. p. 73—76°/11·5 mm. It has D^{20} 0·8823, n_D^{20} 1·4387, α_D −7°. Its *semicarbazone* has m. p. 176°. When reduced by sodium amalgam it yields an *alcohol*, $C_{10}H_{20}O$, b. p. 87—89°/11·5 mm., D^{20} 0·8707, n_D^{20} 1·4507, $[\alpha]_D^{20}$ −6°. This, on treatment with phosphorus pentachloride, passes into the corresponding *chloride* (b. p. 70—73°/10 mm., D^{20} 0·882), which, when heated with quinoline, yields the *hydrocarbon*, $C_{10}H_{16}$. The latter has b. p. 50—54°/11·5 mm., D^{20} 0·812, n_D^{20} 1·4410, α_D^{20} −6°. When oxidised by bromine in alkaline solution, the ketone yields carbon tetrabromide, together with a *monobasic acid*, $C_9H_{16}O_2$, b. p. 131—133°/13·5 mm., D^{23} 0·9773, n_D^{20} 1·4500, α_D^{20} −7°, the *silver* salt of which had m. p. 219°, after darkening at about 160°. The *methyl* ester has b. p. 86—89°/15 mm., D^{23} 0·9208, n_D^{20} 1·4360, α_D^{20} −5·5°. The *amide* has m. p. 114°. On oxidation with nitric acid, the ketone yields an *acid*, $C_8H_{14}O_2$, b. p. 119—122°/12 mm., D^{20} 0·972, n_D^{20} 1·4457, α_D^{20} +7·5°. This yielded a *methyl* ester of b. p. 69—73°/15 mm., D^{20} 0·9359, n_D^{20} 1·4307, α_D^{20} +22°, and an *amide*, m. p. 115—116°. The formation of these compounds is represented by the scheme on p. 122.

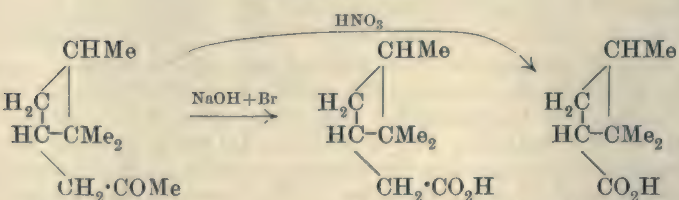
The *diketone*, $C_{12}H_{20}O_2$, after treatment with permanganate to destroy any aldehyde present, is a colourless, mobile oil, b. p. 137—142°/9 mm., D^{20} 0·9600, n_D^{20} 1·4677, α_D^{20} +34°. The b. p. was unaltered by a second treatment with permanganate, whilst the following values were found for the remaining constants: D^{20} 0·9598, n_D 1·4622, α_D +39°. Its *semicarbazone* had m. p. 219°. On oxidation with nitric acid, the diketone yields dimethylsuccinic acid and caryophyllenic acid. Oxidation with bromine in alkaline solution leads to the same products.

The *diketo-aldehyde*, $C_{14}H_{22}O_3$, is a viscous, yellowish-green oil of

b. p. 181—184°/13 mm., D^{20} 1·0280, n_D^{20} 1·4774, α_D^{20} −25°. It does not yield a uniform semicarbazone. When oxidised with permanganate, it yields the acid $C_{14}H_{22}O_4$ (see above). Nitric acid converts it into succinic acid and caryophyllenic acid.



terp.-Caryophyllene.



Ketone, $C_{10}H_{18}O$. Acid, $C_9H_{16}O_2$. Acid, $C_8H_{14}O_2$.

Deussen's caryophyllene was converted into caryophyllene dihydrochloride, which, on treatment with methyl-alcoholic potassium hydroxide, yielded the previously-described "recovered" dextrorotatory caryophyllene (Abstr., 1911, i, 73). An attempt to transform this, through the nitrosite, into Deussen's lævorotatory caryophenyllene was unsuccessful.

Reduction of the blue nitrosite (Deussen, Abstr., 1907, i, 945) led to the formation of a *substance*, $C_{15}H_{27}N$, which is probably an amine. It has b. p. 148—150°/13 mm., D^{20} 0·9297, α_D^{20} +13°, n_D^{20} 1·5030.

H. W.

New Philippine Essential Oils. BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1911, 6, 333—351. Compare Abstr., 1911, i, 1000).—The essential oil from the flowers of *Michelia longifolia* contains linalool, eugenol methyl ether, and methylbutyric and acetic acids, and a very small percentage of thymol.

The leaves of *Toddalia asiatica* (L.) (*T. Aculeata Pers.*, Kurz) yield 0·08% of an essential oil, which gave the following constants: n_D^{30} 1·4620, D_{30}^{30} 0·9059. The oil is largely linalool, but also contains a white, crystalline, camphor-like compound, m. p. 96·5—97°, which is very unstable.

The leaves of *Clausena anisum olens* yield 1·20% of an essential oil with the following constants: n_D^{30} 1·5235 D_{30}^{30} 0·963, ester number 3·6. It contains chavicol methyl ether to the extent of 93%.

About 0·2% of an essential oil with D_{30}^{30} 0·850 is obtainable from the leaves of *Limnophila sp.*

Orange-peel oils were also examined, the *naranjita* variety giving a much greater yield than the *cajel*. The two oils resemble one

another very closely, the former having constants: n_D^{30} 1·4700, $[\alpha]_D^{30}$ 90·85°, ester number 8·0; the latter, n_D^{30} 1·4675, D_{30}^{30} 0·8390, ester number 8·5.

The leaves of *Citrus decumana* yield 1·7% of an essential oil, with constants: n_D^{30} 1·4644, D_{30}^{30} 0·8700, $[\alpha]_D^{30}$ 22·90°, ester number 10. It contains dipentene and linalool and a trace of an aldehyde.

The oil from the leaves of *Citrus hystrix* has the following constants: n_D^{30} 1·4650, D_{30}^{30} 0·9150, $[\alpha]_D^{30}$ −10·50°, ester number 50·2. W. G.

The Essential Oil of Seseli bocconi. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 481—486).—The essential oil of this plant has been obtained by distilling it in steam. By fractional distillation of the oil a number of fractions were isolated, of which the more volatile consist of terpenes, *l*-pinene and *β*-phellandrene having been identified. The oil also contains compounds with carbonyl groups (probably aldehydes), and ethers and alcohols are also present. R. V. S.

Chemistry of Caoutchouc. III. Theory of Vulcanisation. II. DAVID SPENCE [with J. H. SCOTT] (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 300—306. Compare Spence and Scott, Abstr., 1911, i, 657).—Further experiments have been made on the extraction of sulphur from vulcanised caoutchouc by treatment for measured time intervals with equal successive quantities of boiling acetone. These show that equilibrium between the adsorbed sulphur and that in the acetone solution is rapidly attained, and this fact is regarded as favourable to the interpretation which has already been given to the exponential form of the extraction curves. From two series of observations made with the same mixture of para-caoutchouc and sulphur which had been subjected to the vulcanising process for different periods of time, it it is found that the proportion of chemically combined sulphur increases with the period of vulcanisation, and that the initial portions of the extraction curves, corresponding with the removal of the free sulphur, are also different in the two cases. When a non-vulcanised mixture of caoutchouc and sulphur is similarly extracted with boiling acetone, the form of the extraction curve obtained is quite different. The removal of the sulphur from the unvulcanised mixture is, however, also a slow process by reason of the inclusion of the free sulphur in the jelly-like mass which the non-vulcanised caoutchouc forms in contact with the boiling acetone.

An extraction experiment with ebonite gave an extraction curve differing from those obtained with samples of vulcanised caoutchouc, but in this case, also, there appears to be a considerable amount of sulphur which is present in the chemically combined form.

H. M. D.

Brazilian Copal. STANISLAUS MACHENBAUM (*Arch. Pharm.*, 1912, **250**, 6—12).—The copal was red to yellow in colour, and was in small pieces, showing a thin, weathered layer. It sintered at 127°, melted completely at 160°, and had the following percentage solubilities in

the solvents named: alcohol 76, acetone 80, alcohol and ether 92, light petroleum 20. The copal gave the following constants: acid numbers (*a*) direct 123·2, (*b*) indirect 128·5; saponification numbers (*a*) cold 136·2, (*b*) hot 144·2.

An ethereal extract of the resin was shaken with ammonium carbonate solution, which (1) extracted two acids, of which one, *brazilcopalic acid*, $C_{24}H_{40}O_3$, m. p. 170—175°, yielded a lead salt insoluble in alcohol, and (2) precipitated a mixture of two acids, of which *one*, m. p. 195—200°, gave a lead salt insoluble in alcohol. Sodium carbonate solution then extracted from the ethereal solution two acids, of which *brazilcopalolic acid*, $C_{22}H_{38}O_2$, m. p. 95—100°, gave an insoluble lead salt. The residual ethereal solution yielded nothing to potassium hydroxide solution, but on steam distillation furnished a volatile oil, boiling chiefly at 245—255°, and a residue of *a-brazilcopaloresen*, as a brownish-yellow, viscid mass.

The portion of the copal insoluble in ether was dissolved in a mixture of alcohol and ether, and extracted with potassium hydroxide solution, which removed a mixture of resin acids. These were dissolved in alcohol, precipitated as lead salts by lead acetate, regenerated, and separated into two portions by treatment with cold alcohol: the soluble portion is *a-brazilcopalinic acid*, $C_{16}H_{30}O_2$, m. p. 180—185°. The solution after extraction with potassium hydroxide contained *β-brazilcopaloresen* and a little volatile oil. All the substances described are amorphous. The acids give phytosterol-like reactions, and their acid numbers are recorded. T. A. H.

Columbia Copal. STANISLAUS MACHENBAUM (*Arch. Pharm.*, 1912, **250**, 13—19).—The copal was in large pieces, and had a slight turpentine-like odour. It sintered at 120°, melted completely at 155°, and had the following percentage solubilities: ether 56, alcohol 78, alcohol and ether 90, light petroleum 18. Its constants were as follows: acid numbers (*a*) direct 105, (*b*) indirect 106·1, saponification numbers (*a*) cold 106·8, (*b*) hot 110·6. An ethereal extract of the resin was extracted with (1) ammonium carbonate solution and (2) sodium carbonate solution. In each case a mixture of two resin acids was extracted, and was separated into its components by solution in alcohol and precipitation by lead acetate. The acid giving an insoluble lead salt alone was examined in each case, the other being viscid and intractable. As in the case of Brazilian copal (preceding abstract), ammonium carbonate precipitated two resin acids from the ethereal extract; of these, the one giving an insoluble lead salt had m. p. 170—175°. That extracted by ammonium carbonate is *columbiacopalic acid*, $C_{22}H_{40}O_3$, m. p. 145—150°. The acid subsequently removed by sodium carbonate is *columbiacopalolic acid*, $C_{22}H_{40}O_2$, m. p. 90°.

The residual ethereal extract contained volatile oil, boiling chiefly at 210—220°, and brown, viscid *a-columbiacopaloresen*. The portion of the crude copal insoluble in ether was dissolved in a mixture of alcohol and ether, and extracted with potassium hydroxide solution, which removed *a-columbiacopalinic acid*, $C_{14}H_{24}O_2$, m. p. 180—185°, soluble in cold alcohol, and *β-columbiacopalinic acid*, $C_9H_{20}O_3$, m. p.

190°, soluble in hot alcohol. *β-Columbiacopaloresen* remained in the solution.

All the products mentioned are amorphous. The acid numbers and phytosterol-like reactions of the resin acids are recorded.

T. A. H.

So-called Chicle Gum. J. E. QUINTUS BOSZ and N. H. COHEN (*Arch. Pharm.*, 1912, **250**, 52—62).—Tschirch and Schereschewski's work on this material (Abstr., 1905, i, 685) has been repeated, and it is shown that their α-chiclalban is α-amyrin acetate, their β-chiclalban is a mixture of esters of lupeol and β-amyrin, their γ-chiclalban contains as its principal constituent a substance, $C_{56}H_{112}O$, $C_{57}H_{114}O$, or $C_{58}H_{116}O$, m. p. 68°, which on admixture with Hesse's β-cerotinone melts at 66—68°, and is possibly identical with that substance (Abstr., 1893, i, 57). Chiclafluavil is a mixture of all the substances mentioned above. On steam distillation, chicle "gum" yielded a minute quantity of an alkaline distillate with an odour of amines, and on hydrolysis by alkalis furnished acetic, hexoic, and cinnamic acids. The portion of the "gum" insoluble in acetone is brittle, and has none of the properties of caoutchouc, so that the properties of chicle "gum," which render it suitable for "chewing gum" manufacture, do not depend on the presence of caoutchouc-like substances. T. A. H.

Occurrence of Chitin. EDMUND O. VON LIPPMANN (*Ber.*, 1911, **44**, 3716—3717).—A colourless, thin, tough skin, forming a light grey, amorphous powder when dry, which collected on the surface of some waste liquors in a sugar factory which had been set aside for several months, is shown to be composed of chitin produced by bacterial action. E. F. A.

Lutein from Yolk of Egg. RICHARD WILLSTÄTTER and HEINRICH H. ESCHER (*Zeitsch. physiol. Chem.*, 1912, **76**, 214—225).—The chemically indifferent yellow pigments of plants and animals are divided into the hydrocarbons of the carrotene group, $C_{40}H_{56}$, soluble in light petroleum, and the oxygen compounds of the xanthophyll group, $C_{40}H_{56}O_2$, soluble in alcohol (Willstätter and Mieg, Abstr., 1907, i, 865). Lycopene, the colouring matter of tomatoes, has been shown (Willstätter and Escher, Abstr., 1910, i, 330) to belong to the carrotene group, and it is now proved that lutein from the yolk of eggs is a xanthophyll isomeric with, and closely related to, that derived from chlorophyll.

The methods of separating lutein from the phosphatides, fats, and cholesterol of the yolk are described: the pure pigment crystallises slowly from carbon disulphide in well formed prisms, or quickly in fire-red conglomerates of pointed, microscopic needles, m. p. 195—196° (corr.). It crystallises from methyl alcohol in prisms with V-shaped indentations, which are amber-yellow with metallic lustre.

Lutein forms an additive compound with iodine in ethereal solution; the *iodide* is a dark violet powder consisting of microscopic, pointed needles. It absorbs oxygen to the extent of 23% of its weight.

In alcoholic solution it shows absorption bands in the blue and indigo-blue, corresponding with those of xanthophyll from leaves, but differing from carrotene. E. F. A.

[Preparation of Thionaphthen Derivatives.] KALLE & Co. (D.R.-P. 239089. Compare Abstr., 1911, i, 666, 667, 1009).—An account of the preparation of substances having the general formula $RS \cdot C_6H_3(S \cdot CH_2 \cdot CO_2H) \cdot CO_2H$, some of which have been previously described (Abstr., 1911, i, 666).

The following new compounds are mentioned:

2-*Carboxy*-5-*methylthiolphenylthiolacetic acid*, yellowish-white needles, m. p. 220° (decomp.).

3-*Keto*-6-*methylthiol*-(1)-*thionaphthen*-2-*carboxylic acid*, a colourless powder, and 3-*keto*-6-*methylthiol*-(1)-*thionaphthen*, glistening needles, m. p. 133—134°. F. M. G. M.

[Preparation of Thionaphthen Derivatives.] KALLE & Co. (D.R.-P. 239092).—*o*-Nitro-*m*-xylidine was diazotised, and converted by the action of potassium cyanide and copper sulphate into 2-*nitro*-m-*xylonitrile*, needles, m. p. 126°; this when heated at 100° during twelve hours with 80% sulphuric acid yielded 6-*nitro*-2 : 4-*dimethylbenzoic acid*, yellow needles, m. p. 180°, and on reduction furnished the corresponding 6-*amino*-2 : 4-*dimethylbenzoic acid*, a yellow, crystalline powder, m. p. 126° (decomp.). The foregoing amino-acid when diazotised, xanthogenated, and treated with chloroacetic acid yielded 4-*carboxy*-m-*xylyl*-5-*thiolacetic acid*, $CO_2H \cdot C_6H_2Me_2 \cdot S \cdot CH_2 \cdot CO_2H$, a microcrystalline powder, m. p. 158—159°, which on fusion with sodium hydroxide furnished *keto*-4 : 6-*dimethylthionaphthencarboxylic acid*, red flakes, and was subsequently converted into *keto*-4 : 6-*dimethylthionaphthen*, needles, m. p. 93°, which rapidly darkens on exposure to light.

F. M. G. M.

[Preparation of Anthraquinonethioxanthones.] FRITZ ULLMANN (D.R.-P. 238983. Compare Abstr., 1911, i, 1010).—*Anthraquinone-thioxanthone*, orange-red leaflets, m. p. 335°, is prepared by heating anthraquinone-1-*o*-thiolbenzoic acid with phosphorus pentachloride in nitrobenzene solution; the anthraquinone-thioxanthone, m. p. 272°, described previously (Abstr., 1910, i, 270) has now been obtained by fusing anthraquinone-2-*o*-thiolbenzoic acid with *p*-toluenesulphonyl chloride at 205°, whilst anthraquinonyl-1 : 5-di-*o*-thiolbenzoic acid and phosphorus pentachloride furnish an *anthraquinonedithioxanthone*, glistening, orange needles, which do not melt at 350°. F. M. G. M.

[Preparation of "Thioindigo" Derivatives.] KALLE & Co. (D.R.-P. 239673).—When 3-oxy-(1)-thionaphthen-2-carboxylic acid and its derivatives containing a free or substituted amino-group in the benzene nucleus are oxidised in either alkaline solution or neutral suspension, they yield "thioindigo" derivatives.

"6 : 6′-*Diaminothioindigo*" was obtained as a brown, flocculent precipitate by the oxidation of an aqueous alkaline solution of 6-amino-

3-oxy-(1)-thionaphthen-2-carboxylic acid with air at 70—80°; other oxidising agents can also be employed. F. M. G. M.

Lysine Platinichloride. MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1912, **76**, 234—237).—The platinichloride of active lysine, when dried over sulphuric acid, has the composition $C_6H_{14}O_2N_2,PtH_2Cl_6,EtOH$, and crystallises in needles more slender and darker than those of the platinichloride of inactive lysine, which forms stouter, paler yellow prisms, having the composition $C_6H_{14}O_2N_2,PtH_2Cl_6$. Racemic and active lysine may be sharply differentiated in this manner.

E. F. A.

Hæmopyrrole. RICHARD WILLSTÄTTER and YASUHIKO ASAHINA (*Ber.*, 1911, **44**, 3707—3710).—Hæmopyrrole from hæmin or from chlorophyll has been shown to contain phyllopyrrole, $C_9H_{15}N$, *iso*-hæmopyrrole, $C_8H_{13}N$, and another base, $C_8H_{13}N$. The constitutions 2 : 3 : 4- and 2 : 4 : 3-dimethylethylpyrrole respectively were ascribed to the two latter compounds (Willstätter and Asahina, this vol., i, 41), but further investigation is necessary, as neither of them proves to be identical with the 2 : 4-dimethyl-3-ethylpyrrole synthesised by Knorr and Hess (Abstr., 1911, i, 1019; compare also Fischer and Bartholomäus, this vol., i, 50).

The synthesis of Knorr and Hess is confirmed; 2 : 4-dimethyl-3-ethylpyrrole has b. p. 84°/10 mm., 197°/710 mm., D_4^{20} 0·913. The *styphnate* forms four-sided prisms, m. p. 136°; the *chloropicrate* gives prisms, m. p. 140°. On oxidation with nitrous acid, methylethylmaleinimideoxime is obtained, crystallising in prisms, m. p. 215—216° (Knorr and Hess give 201°).

The pyrrole base was reduced with hydrogen iodide and phosphorus at 240°, and finally with platinum and hydrogen. The *pyrrolidine* obtained has b. p. 145°, and forms a *platinichloride*, crystallising in pointed prisms, m. p. 220°, and an *a-naphthylcarbamide*, crystallising in irregularly-defined, rhombic plates, m. p. 109—110°. It is essentially different from *iso*hæmopyrrolidine. E. F. A.

Asymmetric Selenites. LUIGI MARINO and V. SQUINTANI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 666—670. Compare Marino, Abstr., 1908, ii, 833).—When absolutely dry, recently sublimed selenious anhydride is mixed with an equimolecular quantity of a solution of pure piperidine in anhydrous benzene cooled with ice, a colourless, crystalline mass is deposited. The reaction is complete in eight or ten hours. The product, after being washed with anhydrous benzene, gives on analysis figures corresponding with the formula $C_5H_{11}N{\cdot}SeO_2$, but allowance has to be made for absorbed water, owing to the extremely hygroscopic nature of the substance. The *compound* has m. p. 70—71°, but traces of water may lower it to 64—65°. It probably reacts with alcohol, but the reaction product has not been isolated. The piperidine group is not involved in the reaction.

R. V. S.

Cyclic Ammonium Bases. JOHANNES GADAMER (*J. pr. Chem.*, 1911, [ii], **84**, 817—820).—A reply to Decker and Kaufman (Abstr.,

1911, i, 807), who erroneously attributed to the author the view that the carbinol bases have in all cases the structure of amino-aldehydes or ketones. F. B.

Action of Methylamine and Aniline on Benzoyldehydracetic Acid. [Mutual Replacement of Ammonia and Amines in Pyridone Derivatives.] PAVEL I. PETRENKO-KRITSCHENKO and JOH. SCHÖTTLE (*Ber.*, 1911, **44**, 3648—3654. Compare Abstr., 1911, i, 1020).—The interaction of benzoyldehydracetic acid with methylamine and aniline has been studied, whereby the *methyl-* and *phenyl-lactams* of benzoyldehydracetic acid have been obtained. These have m. p. 188° and 203° respectively. Unlike the lactam described previously (*loc. cit.*), neither of these compounds yields a pyridonecarboxylic acid when warmed with alkali. The methyl-lactam, on treatment with hydrochloric acid, yielded 2 : 6-diphenyl-4-pyridone, the *platinichloride* of which, m. p. 218—221° (decomp.), was analysed. When similarly treated, the phenyl-lactam yielded 2 : 6-diphenyl-1 : 4-pyridone.

The methyl- and phenyl-lactams were also prepared by the action of alcoholic solutions of methylamine and aniline on the lactam. Conversely, the methyl-lactam, when treated with alcoholic ammonia, yields the lactam which was identified by conversion into 2 : 6-diphenyl-4-pyridone-3-carboxylic acid and 2 : 6-diphenyl-4-pyridone; on treatment with an alcoholic solution of aniline, it yields the phenyl-lactam.

Similarly, the anilino-group of the phenyl-lactam is replaceable under the action of ammonia or methylamine. H. W.

The Condensation of Acetonedicarboxylic Ester with Aldehydes, Ammonia, and Amines. PAVEL I. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1912, [ii], **85**, 1—37).—A résumé of the results of already published investigations by the author and various co-workers (Abstr., 1906, i, 452; 1907, i, 708; 1908, i, 564; 1909, i, 605, 959; 1910, i, 188). D. F. T.

Preparation of Derivatives and Homologues of Indole. GESELLSCHAFT FÜR TEERVERWERTUNG (D.R.-P. 238138).—When arylhydrazones (or their keto- or aldehyde derivatives) are heated with zinc chloride they furnish indole derivatives. 2-Methylindole was obtained in 75% yield by heating acetonephenylhydrazone (1 part) in 3 parts of solvent naphtha with zinc chloride (1 part) at 150° during one hour, extracting with water, and subsequently fractionating in a vacuum.

3-Methylindole, previously prepared by E. Fischer in 38% yield, was produced in 80% yield from propionaldehydephenylhydrazone at 200°, whilst ethyl phenylhydrazonepyruvate furnished a 60% yield of 2-indolecarboxylic acid at 130°. F. M. G. M.

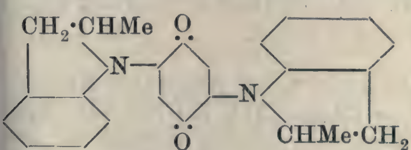
New Synthesis of Benzylidine-2-methylquinoline. VON ISMAILSKY (*J. pr. Chem.*, 1912, [ii], **85**, 90—92).—In the presence of sodium hydroxide solution, *o*-aminobenzaldehyde slowly condenses with excess of styryl methyl ketone, yielding benzylidene-2-methyl quinoline. The product agrees entirely with previous descriptions

(Wallach and Wüsten, Abstr., 1883, 1096; Jacobsen and Reimer, Abstr., 1884, 335; Doebner and Peters, Abstr., 1890, 176; Eibner, Abstr., 1901, i, 64). D. F. T.

Condensation of para-Quinones with Indoles and Pyrroles Containing Hydrogen in the 3-Position. RICHARD MÖHLAU and ALFRED REDLICH *Ber.*, 1911, **44**, 3605—3618).—2-Methylindole and *p*-benzoquinone (2 mols.) react in boiling alcohol to form *2-methylindyl-3-benzoquinone*, $CH<{CH\cdot CO \atop CO\cdot CH}>C{-}C<{CMe \atop C_6H_4}>NH$, dark violet, bronze needles, m. p. about 185°, and quinol in quantitative yield. That the reaction occurs directly at the 3-hydrogen atom, not at the iminic hydrogen atom, is proved, not only by the fact that the colourless *leuco*-compound, obtained by the action of hydrazine hydrate, forms a *diacetate*, m. p. 132° (a triacetate should be formed had the reaction occurred in position 1), but also because 1 : 2-dimethylindole and *p*-benzoquinone yield in a similar manner an almost quantitative amount of 1 : *2-dimethylindyl-3-benzoquinone*, $C_{16}H_{13}O_2N$, m. p. about 160°, violet-black needles. In a similar manner, 2-methylindole and toluquinone yield a corresponding *substance*, $C_{16}H_{13}O_2N$, m. p. about 195° (decomp.), reddish-violet needles; the colourless *diacetate* of its leuco-compound has m. p. 146°. 2-Phenylindole and *p*-benzoquinone give about 40% of *2-phenylindyl-3-benzoquinone*, $C_{20}H_{13}O_2N$, m. p. about 205°, blue needles; 2:5-dimethylindole reacts with *p*-benzoquinone and with toluquinone to form about 90% of *2:5-dimethylindyl-3-benzoquinone*, $C_{16}H_{13}O_2N$, m. p. about 201° (decomp.), violet-black, bronze needles, and 2 : *5-dimethylindyl-3-toluquinone*, $C_{17}H_{15}O_2N$, reddish-violet needles.

As is to be expected from the preceding, pyrroles unsubstituted in positions 3 and 4 react with *p*-quinones (4 mols., two of which are utilised in oxidising the initially-formed leuco-compound) to form diquinonylpyrroles; thus 2 : 5-dimethylpyrrole yields 3 : *4-diquinonyl-2 : 3-dimethylpyrrole*, $NH<{CMe:C\cdot C_6H_4O_2 \atop CMe:C\cdot C_6H_4O_2}$, black, microcrystalline powder, whilst 5-phenyl-2-methylpyrrole yields 3 : *4-diquinonyl-5-phenyl-2-methylpyrrole*, $C_{23}H_{15}O_4N$, brownish-black powder.

Whilst with the preceding indoles and pyrroles only one nucleus enters the benzoquinone molecule, it is found that the more strongly basic 2-methyldihydroindole reacts like the following bases with *p*-quinones, in that two nuclei enter the quinone molecule; thus 2-methyldihydroindole yields a *substance* (annexed formula), m. p. 187°, brown needles; methylaniline yields *bismethylanilinoquinone*,



$$(NPhMe)_2C_6H_2O_2,$$

reddish-brown leaflets; tetrahydroquinoline yields *bistetrahydroquinolinoquinone*, $(C_9NH_{10})_2C_6H_2O_2$, m. p. 189°, brown needles, and 4-methyltetrahydroquinoline yields *bis-6-methyltetrahydroquinolinoquinone*, $(C_9H_9MeN)_2C_6H_2O_2$, m. p. 197°. C. S.

Products of the Condensation of 9-Methylcarbazole and Phthalic Anhydride. FRANZ EHRENREICH (*Monatsh.*, 1911, **32**, 1103—1114. Compare Scholl and Neovius, Abstr., 1911, i, 567).—By the interaction of molecular proportions of 9-methylcarbazole and phthalic anhydride, the main product is 9-methylcarbazole-3-phthaloylic acid, $C_6H_4 \overline{<_{NMe}>} C_6H_3 \cdot CO \cdot C_6H_4 \cdot CO_2H$, together with small quantities of 9-methylcarbazole-3 : 6-diphthaloylic acid,

$$CO_2H \cdot C_6H_4 \cdot CO \cdot C_6H_3 \overline{<_{NMe}>} C_6H_3 \cdot CO \cdot C_6H_4 \cdot CO_2H.$$

When twice as much phthalic anhydride is used, the quantity of the latter is increased considerably.

9-Methylcarbazole is conveniently prepared by the action of methyl iodide or of methyl sulphate at the ordinary temperature on potassium carbazole.

9-*Methylcarbazole*-3-*phthaloylic acid*, prepared by the interaction of the components in benzene solution with aluminium chloride, crystallises in large, well-formed rhombs, m. p. 232°; it shows a characteristic, cherry-red coloration with concentrated sulphuric acid, changing to green on the addition of strong nitric acid. The methyl group is only very slowly and partly eliminated on boiling with hydrogen iodide, and the attraction of alkyl to nitrogen is apparently increased by the phthaloyl group; indeed, no trace of halogen alkyl is obtained on heating the diphthaloyl derivative with hydrogen iodide.

The same *methyl* ester is obtained from the silver salt and methyl iodide, or from the acid chloride and methyl alcohol; it crystallises in monoclinic prisms, m. p. 146°.

9-*Methylcarbazole*-3 : 6-*diphthaloylic acid* crystallises in slender needles, m. p. 330°; the cherry-red coloration with sulphuric acid turns yellow on the addition of strong nitric acid.

The *dimethyl* ester crystallises in large, colourless prisms, m. p. 196°.

2 : 3 : 6 : 7-*Diphthaloyl*-9-*methylcarbazole*,

$$C_6H_4 <_{CO}^{CO}> C_6H_2 \overline{<_{NMe}>} C_6H_2 <_{CO}^{CO}> C_6H_4,$$

prepared by heating 9-methylcarbazole-3 : 6-diphthaloylic acid with sulphuric acid at 90° (compare Scholl and Neovius, *loc. cit.*), crystallises in reddish-yellow plates, which have not melted at 400°. With concentrated sulphuric acid a bluish-violet solution is obtained, which becomes orange when strong nitric acid is added. E. F. A.

Ester Acids of Thiocarboxylic Acids with Aliphatic Alcohol Acids. V. BROR HOLMBERG (*J. pr. Chem.*, 1911, [ii], **84**, 634—686. Compare Abstr., 1910, i, 361, 834).—A detailed account of the action of amines towards the following acids: xanthoacetic acid, $OEt \cdot CS \cdot S \cdot CH_2 \cdot CO_2H$; ethyl dithiocarboglycollic acid,

$$SEt \cdot CS \cdot O \cdot CH_2 \cdot CO_2H;$$

dithiocarbodiglycollic acid, $CO_2H \cdot CH_2 \cdot S \cdot CS \cdot O \cdot CH_2 \cdot CO_2H$; carbodithioglycollic acid, $CO(S \cdot CH_2 \cdot CO_2H)_2$, and trithiocarbodiglycollic acid, $CS(S \cdot CH_2 \cdot CO_2H)_2$.

The previously-observed formation of diphenylcarbamide by the action of aniline on xanthoacetic acid is considered by the author to

be due to the intermediate formation and decomposition of an additive compound with aniline, according to the following scheme:

$$CO_2H\cdot CH_2\cdot S\cdot CS\cdot OEt \rightarrow CO_2H\cdot CH_2\cdot S\cdot C(S\cdot NH_3Ph)(NHPh)\cdot OEt$$
$$\rightarrow CO_2H\cdot CH_2\cdot SH + EtOH + H_2S + CO(NHPh)_2.$$

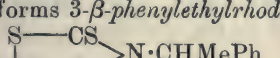
Evidence in support of the author's view is furnished (1) by the non-formation of diphenylcarbamide in acid solution and in the absence of excess of aniline, and (2) by the isolation of similar additive compounds of the thiocarbamylglycollic acids with amines (see below).

β-Phenylethylamine reacts with xanthoacetic acid, yielding an oily *thiourethane*, $CHMePh\cdot NH\cdot CS\cdot OEt$.

Ethyl dithiocarboglycollic acid forms with aniline in aqueous solution the *aniline* salt, $SEt\cdot CS\cdot O\cdot CO_2\cdot NH_3Ph$, m. p. 77·5—78°; when heated with aniline in alcoholic solution, diphenylcarbamide is produced.

Dithiocarbodiglycollic acid reacts with ethylamine to form ethylthiocarbamylthioglycollic acid and the anhydride of ethylthiocarbamylglycollic acid mentioned below. With aniline in ethereal solution it yields the *aniline* salts, $C_5H_6O_5S_2,2NH_2Ph$, lustrous, pale yellow leaflets, m. p. 97—97·5°, and $C_5H_6O_5S_2,NH_2Ph$, m. p. 110—110·5°. When heated with aniline in aqueous solution, dithiocarbodiglycollic acid gives rise to a mixture of substances, the nature of which depends on the ratio of aniline to acid, and the temperature and duration of the reaction; the following compounds were isolated from the product: *s*-diphenylthiocarbamide, phenylrhodanine, trithiocarbodiglycollic acid, glycollic acid, thioglycollic acid, phenylthiocarbamylglycollic acid and its anhydride, and phenylthiocarbamylglycollanilide.

Trithiocarbodiglycollic acid reacts with primary amines, yielding thioglycollic acid and rhodanines (compare Abstr., 1910, i, 361); with β-phenylethylamine it forms 3-β-*phenylethylrhodanine*,

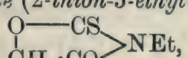


pale yellow, tabular crystals, m. p. 111—112°.

Ethyltrithiocarboglycollic acid and aniline in aqueous solution yield phenylrhodanine and ethyl trithiocarbonate.

N-Substituted derivatives of thiocarbamylglycollic acid are readily obtained by the interaction of amines and ethyldithiocarboglycollic acid.

Ethylthiocarbamylglycollic acid, $NHEt\cdot CS\cdot O\cdot CH_2\cdot CO_2H$, prepared from ethylamine in aqueous solution, crystallises in stellar aggregates of small, white needles, m. p. 97·5—98°; the *sodium* salt is amorphous; the *barium* salt, $(NHEt\cdot CS\cdot O\cdot CH_2\cdot CO_2)_2Ba,3H_2O$, forms colourless plates. It is oxidised by bromine to *ethylcarbamylglycollic acid*, colourless prisms, m. p. 85—86°, and when warmed in aqueous solution forms an *anhydride* (2-*thion*-3-*ethyl*-4-*oxazolidone*),



which crystallises in colourless plates, m. p. 40—40·5°.

Diethylthiocarbamylglycollic acid, $NEt_2\cdot CS\cdot O\cdot CH_2\cdot CO_2H$, prepared from diethylamine, crystallises in flat, colourless prisms, m. p. 90·5—91°,

and yields crystalline *sodium* and *barium* salts; the *ethyl* ester is an oil.

Phenylthiocarbamylglycollic acid, $NHPh\cdot CS\cdot O\cdot CH_2\cdot CO_2H$, m. p. 111—112°, obtained together with phenylrhodanine and diphenylcarbamide by heating aniline with ethyldithiocarboglycollic acid in aqueous solution, crystallises with one molecule of acetic acid in long, colourless prisms, which lose their acetic acid on exposure to air; the *sodium* salt and *barium* salt, $(NHPh\cdot CS\cdot O\cdot CH_2\cdot CO_2)Ba,3H_2O$, were analysed. It readily loses water, forming the *anhydride* (*2-thion-3-phenyl-4-oxazolidone*), $\begin{array}{l}O\text{——}CS\\ CH_2\cdot CO\end{array}\!\!>\!NPh$, which crystallises in stout, irregular plates or short prisms, m. p. 172—173°, and dissolves in aqueous sodium carbonate to form the sodium salt of the original acid. When heated in neutral or alkaline solution, it yields glycollic acid and diphenylcarbamide; in aqueous ammonia, phenylthiocarbamide is produced. Oxidation with potassium permanganate yields phenylcarbamylglycollic acid.

Phenylthiocarbamylglycollanilide, $NHPh\cdot CS\cdot O\cdot CH_2\cdot CO\cdot NHPh$, prepared by heating the acid with aniline in aqueous solution, forms lustrous, white needles, m. p. 133—134°.

2 - Thion - 3 - phenyl - 4 - oxazolidone is oxidised by bromine to 2 : 4-diketo-3-phenyloxazolidine. When dissolved in alcoholic sodium ethoxide, it forms a gelatinous *sodium* salt, $\begin{array}{l}CO\cdot NPh\\ CH_2\text{—}O\end{array}\!\!>\!C(SNa)\cdot OEt$, which is decomposed by acetic acid, yielding *2-ethoxy-2-thiol-3-phenyl-4-oxazolidone*, $\begin{array}{l}CO\cdot NPh\\ CH_2\text{—}O\end{array}\!\!>\!C(SH)\cdot OEt$. This crystallises in colourless needles, m. p. 73—73·5°, and dissolves in alkalis, forming salts of phenylthiocarbamylglycollic acid. The above-mentioned sodium compound reacts with ethyl iodide, yielding a reddish-yellow *oil*, probably $\begin{array}{l}CO\cdot NPh\\ CH_2\text{—}O\end{array}\!\!>\!C(SEt)\cdot OEt$, which, on treatment with aqueous sodium hydroxide, is converted into ethyl mercaptan and phenylcarbamylglycollic acid; with ethyl chloroacetate it forms the *compound*,

$$\begin{array}{l}CO\cdot NPh\\ CH_2\text{—}O\end{array}\!\!>\!C(OEt)\cdot S\cdot CH_2\cdot CO_2Et,$$

which, by dilute hydrochloric acid, is hydrolysed and converted into 2 : 4-diketo-3-phenylthiazolidine, and by acetic acid is hydrolysed to phenylcarbamylglycollic acid and a substance crystallising in small, flat prisms or white needles, m. p. 171—172°. The latter substance is probably *diphenylisohydantoin*, $\begin{array}{l}CO\cdot NPh\\ CH_2\text{—}O\end{array}\!\!>\!C\colon NPh$.

The interaction of chloroacetanilide and the sodium salt of 2-thiol-2-ethoxy-3-phenyl-4-oxazolidone yields a thiazolidone *compound*, $\begin{array}{l}CH_2\text{—}S\\ CO\cdot NPh\end{array}\!\!>\!C\colon NPh$ or $\begin{array}{l}S\text{—}CH_2\\ CO\cdot NPh\end{array}\!\!>\!C\colon NPh$, which forms pale yellow crystals, m. p. 174—175°.

The prolonged action of alcoholic sodium ethoxide on 2-thion-3-phenyl-4-oxazolidone at the ordinary temperature gives rise to

sodium phenylthiocarbamylglycollate; at 100°, xanthanilide is produced.

Piperidine combines with 2-thion-3-ethyl-4-oxazolidone in alcoholic solution to form *2-thiol-2-piperidyl-3-ethyl-4-oxazolidone*, $\begin{matrix}CO\cdot NEt \\ | \\ CH_2—O\end{matrix}\!>\!C(SH)\cdot N\colon C_5H_{10}$, colourless prisms, m. p. 146—147°, and with the corresponding phenyl derivative, yielding *2-thiol-2-piperidyl-3-phenyl-4-oxazolidone*, $\begin{matrix}CO\cdot NPh \\ | \\ CH_2—O\end{matrix}\!>\!C(SH)\cdot C_5NH_{10}$, which forms white needles, m. p. 130—132°.

2-Thion-3-ethyl-4-oxazolidone condenses with benzaldehyde in the presence of sodium ethoxide, yielding α-keto-βγ-diphenylbutyrolactone (Erlenmeyer and Knight, Abstr., 1894, i, 592); the same compound, accompanied by *s*-diphenylthiocarbamide, is obtained by the condensation of 2-thion-3-phenyl-4-oxazolidone with benzaldehyde by sodium ethoxide.

2-Thion-5-benzylidene-3-ethyl-4-oxazolidone, $\begin{matrix}NEt\cdot CO \\ | \\ CS—O\end{matrix}\!>\!C\colon CHPh$, prepared by condensing 2-thion-3-ethyl-4-oxazolidone with benzaldehyde in the presence of piperidine, crystallises in colourless plates or short prisms, m. p. 94·5—95°; when the condensation is effected by means of acetic anhydride, a *stereoisomeride*, crystallising in long, pale yellow prisms, m. p. 137·5—138°, is obtained.

2-Thion-3-phenyl-5-benzylidene-4-oxazolidone,

$$\begin{matrix}NPh\cdot CO \\ | \\ CS—O\end{matrix}\!>\!C\colon CHPh,$$

prepared by condensing 2-thion-3-phenyl-4-oxazolidone and benzaldehyde by means of acetic anhydride, forms slender, golden-yellow needles, m. p. 181·5—182°.

3-Phenylrhodanine reacts with piperidine in alcoholic solution, yielding *phenylpiperidylthiocarbamide*, $NHPh\cdot CS\cdot C_5NH_{10}$, thin, white prisms, m. p. 100—100·5°, and with alcoholic sodium ethoxide to form a *sodium* salt, which on acidification with acetic acid yields *4-keto-2-thiol-2-ethoxy-3-phenylthiazolidine*, $\begin{matrix}CO\cdot NPh \\ | \\ CH_2—S\end{matrix}\!>\!C(SH)\cdot OEt$; this crystallises in colourless, flat, prismatic needles, m. p. 61·5—62°.

The formation of the latter compound furnishes additional evidence in support of the thiazolidine formula assigned to the rhodanines.

F. B.

Nitro-derivatives and Nitro-hydrazones. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 578—583. Compare Hantzsch, Abstr., 1910, i, 475).—The author refers to the different coloured modifications of hydrazones of nitro-aromatic aldehydes which he has described, and suggests that they are chromo-isomerides like the nitroanilines of Hantzsch. According to him, a nitrohydrazone of the formula $NO_2Ar\cdot CH\colon N\cdot NRPh$ can exist in the two forms:

$$O_2N\cdot Ar\cdot CH\colon N\cdot NPhR \text{ (red) and } O_2N\cdot Ar\cdot CH\colon N\cdot NPhR \text{ (yellow).}$$

Since the hydrazones contain a $-C\colon N-$ linking, they can exist in

syn- and *anti*-forms, and it is suggested that the red isomerides are the *syn*-forms, because that configuration would favour the origin of the internal additive product containing a secondary valence.

R. V. S.

Constitution of Buchner's so-called Pyrazolinecarboxylic Acids. CARL BÜLOW (*Ber.*, 1911, 44, 3710—3716).—By the interaction of phenylhydrazine and acraldehyde, Fischer and Knoevenagel obtained phenylpyrazoline, $NPh<\begin{matrix}N=CH\\ CH_2\cdot CH_2\end{matrix}$. Subsequently pyrazoline, $NH<\begin{matrix}N=CH\\ CH_2\cdot CH_2\end{matrix}$, was obtained by Curtius and Wirsing by the interaction of hydrazine and acraldehyde. This is very unstable towards oxidising agents, but it can be distilled unchanged, and is stable towards hydrochloric acid.

On the other hand, the pyrazolinecarboxylic acids described by Buchner (Abstr., 1893, i, 430; 1894, i, 348), obtained from aliphatic diazo-compounds and unsaturated mono- or di-carboxylic acids of the ethylene series, are characterised by giving up all their nitrogen on heating or distillation and forming *cyclo*propanecarboxylic acids. When boiled with dilute mineral acids, hydrazine is eliminated. Lastly, they are readily converted into pyrazole derivatives.

These facts are not in agreement with the relatively stable nature of heterocyclic five-membered rings, and it is considered that Buchner's cids are more correctly formulated as mixed azines of glyoxylic and oxalacetic acid esters; thus the product from ethyl diazoacetate and ethyl fumarate has the formula

$$CO_2Me\cdot CH{:}N\cdot N{:}C(CO_2Me)\cdot CH_2\cdot CO_2Me.$$

Azines such as benzylideneazine, $CHPh{:}N\cdot N{:}CHPh$, give up the whole of their nitrogen on heating, and the other properties of Buchner's acids are shown to be in accord with formulating them as mixed azines instead of as pyrazolinecarboxylic acids. E. F. A.

Pyrimidines. LIV. Condensation of Carbamide and Guanidine with Esters of Allylmalonic and Some Alkyl-substituted Allylmalonic Acids. TREAT B. JOHNSON and ARTHUR J. HILL (*Amer. Chem. J.*, 1911, 46, 537—549).—In an earlier paper (Abstr., 1911, i, 502) it has been shown that ethyl allylmalonate reacts with thiocarbamide to form ethyl 2-amino-4-keto-7-methyltetrahydrohexathiazole-5-carboxylate instead of the expected allylthiobarbituric acid, whilst ethyl benzylallylmalonate and diallylmalonate condense with thiocarbamide with production of acylthiocarbamides or their γ-lactones. In view of this abnormal behaviour, experiments have been carried out to ascertain whether barbituric acid derivatives are formed by the condensation of ethyl allylmalonates with carbamide and guanidine.

5-*Allylmalonylcarbamide* (*allylbarbituric acid*),

$$CO<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CH{:}CH_2,$$

m. p. 167°, obtained by the action of carbamide on ethyl malonate in

presence of sodium ethoxide, crystallises in nearly colourless plates, and is hydrolysed by potassium hydroxide with formation of allylmalonic acid. 5-*Allylmalonylguanidine*,

$$NH:C<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>CH\cdot CH_2\cdot CH:CH_2,2H_2O,$$

m. p. 265—266°, crystallises in pink prisms or hexagonal tablets.

5 : 5-*Diallylmalonylcarbamide* (*diallylbarbituric acid*),

$$CO<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>C(CH_2\cdot CH:CH_2)_2,$$

m. p. 173°, obtained by the action of carbamide on ethyl diallylmalonate, forms colourless, rhombohedral crystals, and on hydrolysis with potassium hydroxide yields diallylmalonic acid. 5 : 5-*Diallylmalonylguanidine*, $NH:C<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>C(CH_2\cdot CH:CH_2)_2$, crystallises in colourless, rhombohedral prisms, does not melt below 300°, and is hydrolysed by potassium hydroxide with formation of diallylmalonic acid.

5-*Benzyl*-5-*allylmalonylcarbamide* (5-*benzyl*-5-*allylbarbituric acid*), $CO<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>C(CH_2Ph)\cdot CH_2\cdot CH:CH_2$, m. p. 198°, prepared by the condensation of carbamide with ethyl benzylallylmalonate, crystallises in prisms; it can also be obtained by the action of allyl iodide on silver benzylbarbiturate. The compound is not hydrolysed smoothly by potassium hydroxide. When guanidine is heated with ethyl benzylallylmalonate in presence of sodium ethoxide, *benzylallyliminomalonuric acid*, $NH_2\cdot C(NH)\cdot NH\cdot CO\cdot C(CH_2Ph)(CH_2\cdot CH:CH_2)\cdot CO_2H$, or, more probably, $NH:C<\genfrac{}{}{0pt}{}{NH\text{——}CO}{NH_3\cdot O\cdot CO}>C(CH_2Ph)\cdot CH_2\cdot CH:CH_2$, is produced, which crystallises in needles, does not melt below 300°, and is immediately transformed by dilute hydrochloric acid into 5-benzyl-5-allylmalonylguanidine *hydrochloride*. 5-*Benzyl*-5-*allylmalonylguanidine*, $NH:C<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>C(CH_2Ph)\cdot CH_2\cdot CH:CH_2$, can also be obtained by the action of benzyl iodide on 5-allylmalonylguanidine; it forms a fine, colourless powder, and does not melt below 300°. Attempts to obtain pure benzylallylmalonic acid by the hydrolysis of this compound with potassium hydroxide were not successful.

Benzylallylmalonic acid, $CH_2:CH\cdot CH_2\cdot C(CH_2Ph)(CO_2H)_2$, was obtained as a viscid, uncrystallisable liquid by the hydrolysis of its ethyl ester with potassium hydroxide; the *silver* salt was prepared.

E. G.

Preparation of 1-*p*-Dimethylaminophenyl-2 : 3 : 4-trimethyl-5-pyrazolone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 238256).—1-p-*Aminophenyl*-2 : 3 : 4-*trimethyl*-5-*pyrazolone*, m. p. 225—227°, prepared by the reduction of 1-*p*-nitrophenyl-2 : 3 : 4-trimethyl-5-pyrazolone, crystallises from water in colourless crystals containing $2H_2O$. When heated at 90—100° with methyl iodide, it yields 1-p-*dimethylaminophenyl*-2:3:4-*trimethyl*-5-*pyrazolone*, which crystallises with $2H_2O$, and has m. p. 140° (anhydrous).

The following compounds are also described: 1-p-*Aminophenyl*-

3 : 4-*dimethyl*-5-*pyrazolone*, a colourless, crystalline powder, m. p. 232°, obtained by reducing the corresponding nitro-compound. 5-*Ethoxy*-1-p-*aminophenyl*-3 : 4-*dimethylpyrazole*, m. p. 95—97°. 1-p-*Acetylaminophenyl*-3 : 4-*dimethyl*-5-*pyrazolone*, a colourless, crystalline powder, m. p. 272—273°. 5-*Ethoxy*-1-p-*acetylaminophenyl*-3 : 4-*dimethylpyrazole*, m. p. 130°. 5-*Acetoxy*-1-p-*acetylaminophenyl*-3 : 4-*dimethylpyrazole*, m. p. 167—168°. 1-p-*Methylaminophenyl*-3 : 4-*dimethyl*-5-*pyrazolone*, needles or leaflets ($1H_2O$), m. p. 108—110°. 1-p-*Dimethylaminophenyl*-3 : 4-*dimethyl*-5-*pyrazolone*, m. p. 199—200°. 1-p-*Acetylmethylaminophenyl*-3 : 4-*dimethyl*-5-*pyrazolone* crystallises with $2H_2O$, m. p. 80° or 162° (anhydrous). 5-*Ethoxy*-1-p-*methylaminophenyl*-3 : 4-*dimethylpyrazole* is an oil; its *nitroso*-derivative has m. p. 75°.

1-p-*Acetylmethylaminophenyl*-2 : 3 : 4-*trimethyl*-5-*pyrazolone* has m. p. 139—140°. 1-p-*Methylaminophenyl*-2 : 3 : 4-*trimethyl*-5-*pyrazolone* has m. p. 168°. F. M. G. M.

[Preparation of Substituted Pyrazolones.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 238373).—It is found that 4-*iso*valerylamino-1-phenyl-3-methyl-5-pyrazolone and its derivatives can be methylated (methyl sulphate) without eliminating the *iso*valeryl group in position 4; the following compounds are described: 4-iso*Valerylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* forms colourless crystals, m. p. 203°. 4-iso*Valerylamino*-1-*phenyl*-3-*methyl*-5-*pyrazolone* forms colourless crystals, m. p. 230°. 4-iso*Valerylamino*-5-*ethoxy*-1-*phenyl*-3-*methylpyrazole* has m. p. 115°. 5-*Chloro*-4-iso*valerylamino*-1-*phenyl*-3-*methylpyrazole* has m. p. 120°. 4-iso*Valerylamino*-5-iso*valeryloxy*-1-*phenyl*-3-*methylpyrazole* has m. p. 122—123°. 4-α-*Bromo*iso*valerylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* forms colourless crystals, m. p. 206°. 4-α-*Bromo*iso*valerylamino*-5-α-*bromo*iso*valeryloxy*-1-*phenyl*-3-*methylpyrazole*, colourless crystals, m. p. 114—116°, is obtained by treating an aqueous solution of 4-amino-1-phenyl-3-methyl-5-pyrazolone hydrochloride with α-bromo*iso*valeryl bromide in the presence of sodium acetate. F. M. G. M.

Hydantoins. VIII. Action of Bromine on Tyrosinehydantoin. TREAT B. JOHNSON and CHARLES HOFFMAN (*Amer. Chem. J.*, 1912, 47, 20—27).—It has been found by Wheeler, Hoffman, and Johnson (Abstr., 1911, i, 923) that tyrosinehydantoin is converted by chlorine into the 3 : 5-dichloro-derivative, and that the latter is hydrolysed by barium hydroxide with formation of 3 : 5-dichlorotyrosine.

It is now shown that iodine reacts in a similar manner with tyrosinehydantoin with production of a nearly theoretical yield of 3 : 5-di-iodotyrosinehydantoin. With bromine, however, tyrosinehydantoin behaves abnormally, giving 3 : 5-dibromobenzylidenehydantoin as the chief product of the reaction, and only a small quantity of 3 : 5-dibromotyrosinehydantoin.

3 : 5-*Di-iodotyrosinehydantoin*, $OH\cdot C_6H_2I_2\cdot CH_2\cdot CH<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, m. p. 235° (decomp.), crystallises in hexagonal plates.

3 : 5-*Dibromo*-4-*hydroxybenzoylhydantoic acid* (3 : 5-*dibromotyrosinehydantoic acid*), $NH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_2Br_2\cdot OH$, m. p.

191°, obtained by the action of potassium cyanate on 3 : 5-dibromotyrosine, forms rhombohedral plates or square prisms, and is hydrolysed by concentrated hydrochloric acid with formation of 3 : 5-*dibromotyrosinehydantoin*, $OH\cdot C_6H_2Br_2\cdot CH_2\cdot CH<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, m. p. 223—225° (decomp.), which crystallises in prisms.

3 : 5-*Dibromo-4-hydroxybenzylidenehydantoin*,

$$OH\cdot C_6H_2Br_2\cdot CH{:}C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix},$$

m. p. above 295° (decomp.), obtained by condensation of 3 : 5-dibromo-4-hydroxybenzaldehyde with hydantoin, forms small, brownish-yellow needles, yields a yellow *ammonium* salt, and is reduced by hydriodic acid with production of 3 : 5-dibromotyrosinehydantoin. 3 : 5-Dibromo-4-hydroxybenzylidenehydantoin is also produced by the action of bromine on tyrosinehydantoin and on 3 : 5-dibromotyrosinehydantoin.

E. G.

The Reduction of Aromatic Aldazines. THEODOR CURTIUS (*J. pr. Chem.*, 1912, [ii], 85, 37—77. Compare Abstr., 1900, i, 610). —The paper first gives a summarised account of the results of the investigations published hitherto by different workers on the products obtained by the reduction of benzaldazine (benzylidenehydrazine) and its substituted derivatives under various conditions.

[With FRANZ SCHNEIDERS.]—Benzylhydrazine easily undergoes atmospheric oxidation, giving a deposit of benzaldehydebenzylhydrazone (private communication from August Darapsky).

Towards the esters of β- and γ-ketonic acids, benzylhydrazine behaves like phenylhydrazine. Warmed with benzoylacetic ester it yields 3-*phenyl*-1-*benzyl*-5-*pyrazolone*, a white, crystalline powder, m. p. 204—205°. Ferric chloride solution is without action on the substance (contrast the 1-benzyl-3-methyl compound below). When treated in glacial acetic acid solution with sodium nitrite, 4-*oximino*-3-*phenyl*-1-*benzyl*-5-*pyrazolone* is obtained; it forms deep red needles, m. p. 161—162°.

On warming benzylhydrazine with ethyl lævulate, 1-*benzyl*-3-*methyl*-6-*pyridazinone*, $CH_2<\begin{matrix}CH_2\cdot CO\\ CMe=N\end{matrix}>N\cdot CH_2Ph$, is obtained; this crystallises from light petroleum in colourless, prismatic crystals, m. p. 56—57°.

When cautiously added to ethyl acetoacetate, benzylhydrazine yields 1-*benzyl*-3-*methyl*-5-*pyrazolone*, a white, crystalline solid, m. p. 175—176°, b. p. 192—194°/14 mm.; the intermediate benzylhydrazone of acetoacetic ester could not be isolated. The product is acid to litmus, and the *copper*, *cobalt*, *nickel*, and *silver* salts are described; the *hydrochloride* forms prismatic crystals, m. p. 120°.

1-Benzyl-3-methyl-5-pyrazolone is exceedingly reactive. Ferric chloride solution in the cold gives a brown coloration, and on boiling causes oxidation to the corresponding pyrazole-blue. Heated with phosphorus pentachloride, it yields 4-*dichloro*-1-*benzyl*-3-*methyl*-5-*pyrazolone*, which crystallises in leaves, m. p. 59—61°; the analogous 4-*dibromo*-compound forms small, hard crystals with a tinge

of yellow (m. p. 81—83°); these two dihalogen compounds are, unlike the original substance, indifferent to both acid and alkali.

4-p-*Tolueneazo*-1-*benzyl*-3-*methyl*-5-*pyrazolone*, obtained by the action of toluenediazonium sulphate, forms slender, yellow needles, m. p. 123—124°.

1-*Benzyl*-4-*benzylidene*-3-*methyl*-5-*pyrazolone*, obtained by the action of benzaldehyde on benzylmethylpyrazolone, forms red crystals, m. p. 111—112°.

On heating benzylmethylpyrazolone with phenylhydrazine, ammonia is evolved, and 4-*bis*-1-*benzyl*-3-*methyl*-5-*pyrazolone*,

$$\begin{array}{r} N{:}CMe \\ CH_2Ph\cdot N{-}CO \end{array}\!\!>CH\cdot CH<\!\!\begin{array}{l} CMe{:}N \\ CO{-}N\cdot CH_2Ph \end{array},$$

obtained, which forms white needle crystals, melting above 330°; by oxidation with various oxidising agents it passes smoothly into 1-*benzyl*-3-*methylpyrazole-blue*, $\begin{array}{r} N{:}CMe \\ CH_2Ph\cdot N{-}CO \end{array}\!\!>C{:}C<\!\!\begin{array}{l} CMe{:}N \\ CO{-}N\cdot CH_2Ph \end{array}$; this crystallises in almost black needles, m. p. 142—144°, and is decomposed by strong acids and boiling alkali solutions. Careful oxidation of benzylmethylpyrazolone by potassium permanganate gives a white acid *substance* of indefinite m. p., which could not be further purified; the *silver* salt was obtained as a white precipitate, m. p. 185—189°; excess of permanganate causes oxidation to benzaldehyde and benzoic acid.

On treating 1-benzyl-3-methyl-5-pyrazolone in dilute hydrochloric acid solution with sodium nitrite, 4-*oximino*-1-*benzyl*-3-*methyl*-5-*pyrazolone* is obtained, crystallising in yellow needles or prisms, m. p. 152—152·5°. By reduction with zinc dust in acetic acid solution, the oximino-compound gives a solution of 4-*amino*-1-*benzyl*-3-*methyl*-5-*pyrazolone*, which was not isolable, and attempts to isolate it as the benzylidene derivative merely caused oxidation to the corresponding *rubazonic acid* of 1-*benzyl*-3-*methyl*-5-*pyrazolone*,

$$\begin{array}{r} N{:}CMe \\ CH_2Ph\cdot N{-}CO \end{array}\!\!>CH\cdot N{:}C<\!\!\begin{array}{l} CMe{:}N \\ CO{-}N\cdot CH_2Ph \end{array};$$

this, more conveniently prepared by oxidation of the amino-compound with ferric chloride, forms cinnabar-red crystals, m. p. 160—161°; its solutions in alkalis are violet-red.

The *ammonium* salt of 4-oximino-1-benzyl-3-methyl-5-pyrazolone forms a yellow powder (m. p. 175—176°); with silver nitrate it yields the *silver* salt as a reddish-brown, insoluble, amorphous powder, which decomposes completely at 179°.

On the other hand, silver nitrate decomposes an acetic acid solution of the free oximino-compound, nitrous fumes are evolved, and finally microscopic needles of the *silver* salt of 4-nitro-1-benzyl-3-methyl-5-pyrazolone are obtained, which decompose at 245—246°.

4-*Nitro*-1-*benzyl*-3-*methyl*-5-*pyrazolone* can be obtained from the silver salt, or by oxidation of the oximino-compounds with nitric acid; it forms colourless needles, m. p. 144—145° (decomp.).

The silver salt of the nitro-compound gives with aniline a *substance*, $\begin{array}{r} N{:}CMe \\ CH_2Ph\cdot N{-}CO \end{array}\!\!>C{:}N(NHPh)_2\cdot OAg$, which separates on cooling in

yellow, capillary crystals; treatment with solvents removes aniline from the substance, regenerating the original silver salt.

1-*Benzyl*-2 : 3-*dimethyl*-5-*pyrazolone* (1-*benzylantipyrine*) is obtained by methylating 1-benzyl-3-methyl-5-pyrazolone. It forms anhydrous, hygroscopic crystals, m. p. 84—86°; from moist solvents, it crystallises with $\frac{1}{2}H_2O$, and then has m. p. 102—103°. The *picrate* forms long, yellow needles (from hot water), m. p. 143—145°. 4-*Oximino*-1-*benzyl*-2 : 3-*dimethylpyrazolone* is an unstable, deep green, viscous oil. If benzylantipyrine is oxidised with concentrated nitric acid, 4-*nitro*-1-*benzyl*-2 : 3-*dimethylpyrazolone* is obtained as colourless, prismatic crystals, m. p. 161—162°.

The physiological action of benzylantipyrine was investigated; it appears to possess certain advantages over ordinary antipyrine.

[With Gustav Sprenger.]—*p*-Methylbenzylhydrazine (compare Abstr., 1900, i, 612) is best prepared by reduction of *p*-methylbenzaldazine by sodium amalgam; on dilution with water and cooling, crystals of the *p*-methylbenzylhydrazone of *p*-tolualdehyde separate, and can be decomposed by hydrochloric acid. The *dihydrochloride*, m. p. 150° (decomp.), the *sulphate*, m. p. 178—179°, and the *oxalate*, m. p. 180°, were obtained.

Benzaldehyde-p-methylbenzylhydrazone forms large, transparent tablets, m. p. 88°; the *diacetyl* derivative, $C_6H_4Me{\cdot}CH_2{\cdot}N_2HAc_2$, forms crystals, m. p. 75° (indefinite). The stable *nitroso*-compound, $C_6H_4Me{\cdot}CH_2{\cdot}N(NO){\cdot}NH_2$, crystallises from water in needles, m. p. 78°, and when warmed with dilute sulphuric acid yields *p*-methylbenzylazoimide, $C_6H_4Me{\cdot}CH_2{\cdot}N_3$, b. p. 94°/12 mm. (compare Curtius and Darapsky, Abstr., 1902, i, 844). With ethyl acetoacetate, *p*-methylbenzylhydrazine gives 1-*p*-methylbenzyl-3-methyl-5-pyrazolone (compare Abstr., 1900, i, 612); its *hydrochloride* has m. p. 130°. By treatment with nitrous acid the above pyrazolone is converted into yellow 4-*oximino*-1-p-*methylbenzyl*-3-*methyl*-5-*pyrazolone*, m. p. 154°. By methylation the pyrazolone is converted into 1-p-*methylbenzyl*-2 : 3-*dimethyl*-5-*pyrazolone*, which forms prismatic crystals, m. p. 78°. The substance behaves analogously to antipyrine and benzylantipyrine towards nitrous acid and ferric chloride. Its physiological effect has not yet been investigated. D. F. T.

Ethyl Cyanoanilide-*o*-carboxylate. Ralph H. McKee (*J. pr. Chem.*, 1911, [ii], **84**, 821—826).—By the interaction of ethyl cyanoimidocarbonate and ethyl anthranilate, Finger and Zeh (Abstr., 1910, i, 382) obtained a compound which they considered to be ethyl cyanoanilide-*o*-carboxylate. The author has investigated the action of cyanogen bromide on ethyl anthranilate, and finds that the resulting compound, which undoubtedly has the structure of ethyl cyanoanilide-*o*-carboxylate, is different from Finger and Zeh's compound. The latter substance is considered to be ethylbenzoylene*iso*carbamide, [2-ethoxyquinazolone], $\begin{matrix}CO{-\!\!-\!\!-}N\\ |\\ C_6H_4{\cdot}NH\end{matrix}\!\!>\!C{\cdot}OEt$ or $\begin{matrix}CO{\cdot}NH\\ |\\ C_6H_4{\cdot}N\end{matrix}\!\!\geqslant\!C{\cdot}OEt$, and this view is supported by the formation of the corresponding methyl compound by the interaction of methyl cyanoimidocarbonate and ethyl anthranilate. According to Finger and Zeh the products obtained

from both the methyl and ethyl cyanoimidocarbonates should be identical. Finger and Günzler had already shown that it is a quinazoline derivative (Abstr., 1911, i, 237).

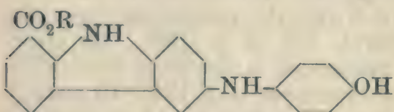
Methyl cyanoimidocarbonate, $NH\!:\!C(CN)\cdot OEt$, prepared by the action of hydrogen chloride on methyl alcohol and potassium cyanide, is a colourless oil, b. p. 115°/760 mm., having an odour of mice excrement. It reacts with ethyl anthranilate at 80° in the presence of cuprous chloride, yielding *2-methoxyquinazolone*, $\begin{matrix} CO\text{——}N \\ | \\ C_6H_4\cdot NH \end{matrix}\!\!>\!C\cdot OMe$, m. p. 231—232° (corr.), which is hydrolysed by hydrochloric acid to 2 : 4-diketodihydroquinazoline, m. p. 357° (corr.); Griess (*Ber.*, 1869, 2, 416) gives 344°.

Methyl cyanoanilide-o-carboxylate, $CN\cdot NH\cdot C_6H_4\cdot CO_2Me$, obtained by the action of cyanogen bromide on methyl anthranilate in ethereal solution, crystallises in needles, m. p. 105° (corr.). When heated at 100°, it polymerises to *tri-o-carbomethoxyphenylmelamine*, $C_{27}H_{24}O_6N_6$, which has m. p. about 160°.

Ethyl cyanoanilide-o-carboxylate, prepared from cyanogen bromide and ethyl anthranilate, has m. p. 93—94°, and polymerises to *tri-o-carbethoxyphenylmelamine*, $C_{30}H_{30}O_6N_6$, m. p. 190° with previous sintering.

Methyl anthranilate forms a *picrate*, $NH_2\cdot C_6H_4\cdot CO_2Me,C_6H_3O_7N_3$, crystallising in deep yellow, microscopic needles, m. p. 106° (corr.); the *picrate* of ethyl anthranilate has m. p. 116° (corr.). F. B.

Preparation of Derivatives of Indophenols. LEOPOLD CASSELLA & Co. (D.R.-P. 238857).—Indophenols prepared from carbazolecarboxylic acids and nitrosophenols have previously been described; these substances on reduction furnish leuco-derivatives having the annexed general constitution,



which, when slowly dropped into a hot solution of sodium polysulphide, yield dark blue sulphur cotton dyes which are extremely fast to light, washing, or chlorine. F. M. G. M.

Preparation of Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 238981. Compare following abstract).—When acyl *o*-diaminoanthraquinones are treated with dehydrating reagents, the following action takes place:

$$A\!<\!\begin{matrix} NR\cdot COR' \\ NH_2 \end{matrix} = A\!<\!\begin{matrix} NR \\ -N \end{matrix}\!\!>\!CR' + H_2O,$$

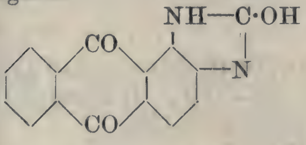
where A is an anthraquinone residue (substituted or otherwise), R hydrogen, alkyl, or aryl, and R′ alkyl, aryl, or an ethoxy-group.

1 : 2-*Phenylanthraquinoneiminazole*, prepared from benzoyl-1 : 2-diaminoanthraquinone, and 4-*amino*-1 : 2-*phenylanthraquinoneiminazole*, obtained from benzoyl-1 : 2 : 4-triaminoanthraquinone by the action of sulphuric acid at 150°, form yellow crystals and glistening, metallic needles respectively.

1 : 2-*Hydroxyanthraquinoneiminazole* (I), prepared by the action of carbonyl chloride on 1 : 2-diaminoanthraquinone, crystallises from quinoline in needles.

4-*Hydroxy*-2-*ethoxy*-1-p-*tolylanthraquinoneiminazole* (II), yellow needles, was obtained by the fusion (at 100°) of *p*-toluidine with dinitro-β-aminoanthraquinoneurethane; it yields a *sulphonic acid* when heated with fuming sulphuric acid.

1:2-*Methylanthraquinoneiminazole*, yellow needles, obtained from 1:2-diaminoanthraquinone and acetic anhydride, and the *compound*, from the same base and formic acid, are also mentioned in the original.



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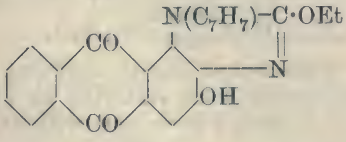


(II.)

F. M. G. M.

Preparation of Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R-P. 238982).—Condensation products of benzaldehyde and β-aminoanthraquinones have been described by Kaufler (Abstr., 1904, i, 207); this condensation is now found to take place readily with *o*-diaminoanthraquinones and either aliphatic or aromatic aldehydes.

The compounds prepared from 1:2-diaminoanthraquinone and 1:2:4-triaminoanthraquinone respectively with benzaldehyde are identical with those obtained from the benzoyl derivatives of these compounds when heated with sulphuric acid (compare preceding abstract), whilst 1:2-diaminoanthraquinone with para-acetaldehyde in concentrated sulphuric acid at 0—10° yields the 1:2-methylanthraquinoneiminazole also previously described. F. M. G. M.

[Preparation of Anthraquinoneacridone Derivatives.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 238977 and 238978).—Anthraquinoneacridone can be conveniently nitrated with nitro-sulphuric acid at 0—5°; the nitrated *product* is yellow, and does not fuse at 300°; when reduced with sodium sulphide at 100°, it furnishes *aminoanthraquinoneacridone* (not melted at 300°).

Benzoylaminoanthraquinoneacridone separates in crystalline form when a nitrobenzene solution of aminoanthraquinoneacridone is boiled with benzoyl chloride; the *acetyl* compound has also been prepared. The second patent states that the foregoing benzoylaminoanthraquinoneacridone can be obtained by boiling a nitrobenzene solution of bromoanthraquinoneacridone with benzamide in the presence of copper and sodium carbonate during twenty-four hours. F. M. G. M.

Nature of the Indanthren Fusion of 2-Aminoanthraquinone: 2-Hydroxylamino- and 2:2′-Azoxyanthraquinone. ROLAND SCHOLL and FRITZ EBERLE (*Monatsh.*, 1911, 32, 1035—1042).—2-Hydroxylaminoanthraquinone, obtained in small quantity by reduction of 2-nitroanthraquinone, could not be converted into indanthren by fusion with an alkali hydroxide. In alkaline solution hydroxylaminoanthraquinone is very readily oxidised by atmospheric

oxygen to 2 : 2′-azoxyanthraquinone. This compound could not be reduced to the corresponding hydrazoanthraquinone, 2-aminoanthraquinone always resulting.

The formation of indanthren from 2-aminoanthraquinone is explained on the assumption that on fusion with an alkali hydroxide 2-aminodihydro-1 : 2′-dianthraquinonylamine,

$$NH_2\cdot C_{14}H_6(OH)_2\cdot NH\cdot C_{14}H_7O_2,$$

is formed, and that this loses hydrogen, forming dihydroindanthren, $C_{14}H_6(OH)_2{<}{}^{NH}_{NH}{>}C_{14}H_6O_2$.

Hydroxylaminoanthraquinone, $C_{14}H_7O_2\cdot NH\cdot OH$, was obtained as an orange-red solid, sintering at 140°, m. p. 158—160°. It dissolves in dilute sodium hydroxide with an intense green coloration.

2:2′-*Azoxyanthraquinone*, $ON_2(C_6H_3{<}{}^{CO}_{CO}{>}C_6H_4)_2$, crystallises in small, light brown prisms and prismatic plates, m. p. 342·5°. The solution in concentrated sulphuric acid is red. A solution in hot acetone gives a very characteristic cornflower-blue coloration on the addition of a few drops of sodium hydroxide. E. F. A.

[Preparation of Dimethylindanthren.] BADISCHE ANILIN & SODA-FABRIK (D.R.-P. 238979).—3 : 3′-*Dimethylindanthren*, a bluish-grey, crystalline powder, can be prepared by boiling an acetic acid solution of 2-amino-3-methylanthraquinone (1 part) with lead peroxide (3 parts) during three hours, or by boiling a naphthalene solution of 1-bromo-2-amino-3-methylanthraquinone with copper oxide and anhydrous sodium acetate during four to five hours. A similar *compound* can be obtained from 2-amino-6(7)-methylanthraquinone.

F. M. G. M.

Action of Semicarbazide on Hydroxamic Acids. HANS RUPE and F. FIEDLER (*J. pr. Chem.*, 1911, [ii], **84**, 809—816).—It has been shown previously (Rupe and Kessler, Abstr., 1910, i, 93) that the action of semicarbazide hydrochloride on aliphatic oximino-ketones leads to the replacement of the oximino-group by the semicarbazide residue, $:N\cdot NH\cdot CO\cdot NH_2$. A similar elimination of the oximino-group is found to take place with hydroxamic acids, resulting in the formation of semicarbazides. The reaction is, however, not a general one. The replacement occurs readily with benzhydroxamic and acethydroxamic acids, and with difficulty in the case of phenylacethydroxamic acid, whilst with salicylhydroxamic and cinnamhydroxamic acids no reaction takes place.

Benzoylsemicarbazide, obtained by heating benzhydroxamic acid with semicarbazide hydrochloride in aqueous solution, has m. p. 215°, and may also be prepared by the action of ethyl benzoate or benzoic anhydride on semicarbazide. The high m. p. (225°) given by Widmann and Cleve (Abstr., 1898, i, 335) is due to the presence of hydrazodicarboxylamide. The *acetyl* derivative, $C_{10}H_{11}O_3N_3$, forms lustrous, white leaflets, m. p. 174°, and is instantly hydrolysed by cold aqueous sodium hydroxide.

Cinnamoylsemicarbazide, $C_{10}H_{11}O_2N_3$, prepared by heating cinnamic

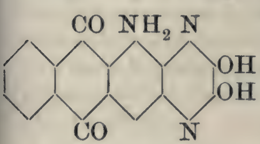
anhydride with semicarbazide, crystallises in needles; the *acetyl* derivative forms slender, white needles, m. p. 177—178°.

Phenylacetylsemicarbazide, $C_9H_{11}O_2N_3$, obtained from the acid chloride or anhydride in a similar manner, or by the interaction of phenylhydroxamic acid and semicarbazide hydrochloride in aqueous solution, crystallises in slender needles, m. p. 167—168°. F. B.

Azines and Quinonediazides of the Anthraquinone Series. ROLAND SCHOLL, FRITZ EBERLE, and WALTER TRITSCH (*Monatsh.*, 1911, **32**, 1043—1056).—(1) *Azines from Triaminoanthraquinone.*—On condensing 1 : 2 : 3-triaminoanthraquinone with *o*-dicarbonyl compounds, azines of entirely different nature are to be expected, according as the pyrazine nucleus becomes attached in the angular 1 : 2-position or the linear 2 : 3-position. The linear derivatives should possess the same properties as the azines from 2 : 3-diaminoanthraquinone (Scholl and Kacér, Abstr., 1905, i, 88), characterised by their giving brown reduction products with alkaline sodium hyposulphite (Scholl and Edlbacher, Abstr., 1911, i, 756).

Oxalic acid, benzil, 1 : 2-naphthaquinone, phenanthraquinone, and isatin yield azines with triaminoanthraquinone, which all form insoluble brown products in alkaline sodium hyposulphite. The azines are accordingly regarded as linear (for nomenclature see Scholl, Abstr., 1911, i, 677). 1 : 2 : 3-Triaminoanthraquinone has m. p. 325° (decomp.).

Dihydroxy-2 : 3-*pyrazino*-1-*aminoanthraquinone* (annexed formula), produced on condensation with oxalic acid, sublimes in lustrous, dark brown needles. It is not melted at 400°; in boiling with dilute sodium hydroxide, it dissolves, giving a red solution, from which a red sodium salt separates on cooling.



Diphenyl-2 : 3-*pyrazino*-1-*aminoanthraquinone*,

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H(NH_2)<\genfrac{}{}{0pt}{}{N:CPh}{N:CPh},$$

prepared by condensation of triaminoanthraquinone and benzil, crystallises in tiny red or brownish-red needles, m. p. 241°; it sublimes without decomposition, and gives a red coloration with concentrated sulphuric acid.

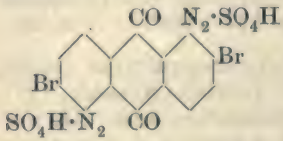
2 : 3(1′ : 2′-)-*Naphthazino*-1(or 4-)-*aminoanthraquinone* is obtained as a dark brown, amorphous compound, m. p. 266—267°.

2 : 3(9′ : 10′-)-*Phenanthrazino*-1-*aminoanthraquinone* crystallises in well formed, reddish-brown, lustrous needles, m. p. 361°.

2 : 3-*Indazino*-1(or 4-)-*aminoanthraquinone* forms a dark brown, indefinitely crystalline powder, m. p. above 400°. When heated with sodium hyposulphite and sodium hydroxide it forms a reddish-brown vat, which dyes cotton yarn light brown.

(2) *Quinoneazides of the Anthraquinone Series.*—The quinonediazides of the anthraquinone series in contrast to those of the benzene series cannot be coupled with naphthol or naphthylamine to azo-dyes. With resorcinol they couple only very slowly on prolonged heating.

2 : 6-*Dibromoanthraquinone*-1 : 5-*bisdiazonium sulphate* (I), produced on diazotising dibromodiaminoanthraquinone, separates in yellowish-red crystals, m. p. 185—186°. When boiled with dilute sulphuric acid it is converted into *anthraquinone*-2 : 1 : 6 : 5-*bisquinonediazide* (II).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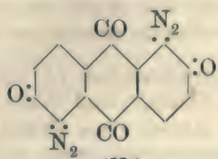
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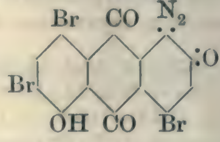
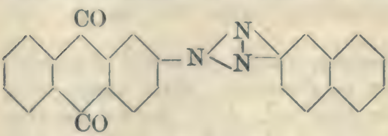

(III.)

This crystallises in well-formed, metallic-green, lustrous crystals, which explode at 156°.

4 : 6 : 8-*Tribromo-5-hydroxyanthraquinone*-2 : 1-*quinonediazide* (III), prepared by diazotising 2 : 4 : 6 : 8-tetrabromo-1 : 5-diaminoanthraquinone and boiling the crude diazo-product, was obtained in a brown, crystalline form from acetone, which blackens and sinters above 360°.

E. F. A.

[Preparation of ψ-Azimino-compounds.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 238253). When the azo-compounds obtained by the combination of β-diazoanthraquinones with β-naphthylamine are oxidised they yield ψ-azimino-compounds, such as *aβ-naphthylene-ψ-azimino-β-anthraquinonyl* (annexed formula). The sulphonic derivatives are soluble in water, and form valuable cotton dyes.



F. M. G. M.

Action of Hydrazoic Acid on Cyanogen. Formation of Cyanotetrazole. E. OLIVERI-MANDALÀ and T. PASSALACQUA (*Gazzetta*, 1911, **41**, ii, 430—435. Compare Oliveri-Mandalà, Abstr., 1910, i, 343; 1911, i, 337; Oliveri-Mandalà and Coppola, Abstr., 1910, i, 593; Oliveri-Mandalà and Alagna, Abstr., 1911, i, 243; Dimroth and Fester, Abstr., 1910, i, 645).—When cyanogen is passed into a 40% aqueous solution of azoimide, *cyanotetrazole* [*tetrazole*-5-*carboxylonitrile*], C_2HN_5, is produced. The substance becomes slightly red at 70° and melts at 99°, forming a reddish-brown liquid. It yields ammonia quantitatively when boiled with potassium hydroxide solution. The *silver* salt, C_2N_5Ag, and the *barium* salt,

$$(C_2N_5)_2Ba,3\tfrac{1}{2}H_2O,$$

were prepared.

When the silver salt of cyanotetrazole is treated with ethyl iodide, 1-*ethyltetrazole*-5-*carboxylonitrile*, $\begin{matrix}C(CN)\cdot NEt\\ | \qquad\qquad \\ N\text{———————}N\end{matrix}\!\!\geqslant\!N$, is obtained; it is a colourless liquid, b. p. 127°/46 mm. On distillation at ordinary pressure, it explodes at about 200°. 1-*Ethyltetrazole*-5-*carboxylamide*, $C_4H_7ON_5$, is prepared by heating at 50—60° an alkaline solution of 1-ethyltetrazole-5-carboxylonitrile with hydrogen peroxide solution;

it crystallises in minute, lustrous scales, m. p. 125—126°. 1-*Ethyltetrazole-5-carboxylic acid*, $C_4H_6O_2N_4$, is obtained by heating 1-ethyltetrazole-5-carboxylonitrile with methyl-alcoholic potassium hydroxide, and neutralising the potassium salt with sulphuric acid. The acid crystallises in acicular prisms, m. p. 124—125°. In addition to the *potassium* salt, $C_4H_5O_2N_4K$, the *silver* salt, $C_4H_5O_2N_4Ag$, was prepared. When 1-ethyltetrazole-5-carboxylic acid is kept at 130—140° it loses carbon dioxide, and 1-ethyltetrazole (identified as platinichloride) is obtained, identical with the *N*-ethyltetrazole formerly described. R. V. S.

Identity of the Guanine Pentoside from Molasses with Vernine. ERNST SCHULZE and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, **76**, 145—147).—Vernine (guanine-*d*-ribose), for which the composition $C_{10}H_{13}O_5N_5,2H_2O$ was recognised by Schulze and Castoro (Abstr., 1904, ii, 506), is identical with the guanosine obtained by Levene and Jacobs from nucleic acid, and with the guaninepentoside isolated by Andrlik (Abstr., 1911, i, 397) from molasses. In 1·5% sulphuric acid it has $[\alpha]_D^{20}$ $-8·4°$. E. F. A.

The Fastness to Light of Hydroxyazo-compounds. Some Derivatives of α-Methoxynaphthalenes. N. WOROSHZOFF (*Zeitsch. Farb.-Ind.*, 1911, **10**, 169—173).—It is found that the alkylation of the hydroxy-group in hydroxyazo-compounds increases the fastness to light of the colouring matters obtained therefrom, and that methylation can be conveniently carried out by shaking an alkaline solution of the compound with methyl sulphate.

Sodium 1-*methoxynaphthalene*-4-*sulphonate*, prepared by shaking α-naphthol-4-sulphonic acid with methyl sulphate in the presence of sodium hydroxide, separates in glistening leaflets.

4-*Nitro*-1-*methoxynaphthalene*, yellow needles, m. p. 81°, is obtained by slowly adding an intimate mixture of the foregoing acid (10 parts) and anhydrous sodium carbonate (0·6 part) in small portions to a cooled solution of 1·5 grams of carbamide in 20 c.c. of nitric acid (D 1·4); on reduction with stannous chloride and hydrochloric acid it furnishes 4-*methoxy-α-naphthylamine hydrochloride* in colourless crystals; the free *base* is a dark oil; its *acetyl* derivative has m. p. 180—181°. F. M. G. M.

Salicylic Acid Azo-dyes. EUGÉNÈ GRANDMOUGIN (*Ber.*, 1911, **44**, 3756).—A claim for priority against Bulow (Abstr., 1911, i, 338). D. F. T.

Decomposition of Azines by Heat. I. and II. PAUL PASCAL and LÉON NORMAND (*Bull. Soc. chim.*, 1911, [iv], **9**, 1029—1037, 1059—1068).—Curtius and Jay (Abstr., 1889, 393) showed that benzaldazine decomposes when heated, forming stilbene, and Bouveault obtained di-*p*-methylstilbene in a similar way from tolualdazine (Abstr., 1897, i, 347, 530), but failed to generalise the reaction. In the first of these papers the authors show that, in general, the aromatic aldazines melt with very slight decomposition, but when the tempera-

ture is raised above the melting point, evolution of gas commences and increases with rise of temperature, the principal reaction being the production of nitrogen and the stilbene corresponding with the aldazine used. At the higher temperatures some ammonia and hydrogen are formed, with, as a solid product, the corresponding phenanthrene, due to loss of H atoms at positions contiguous to the azine side-chain. The rate of decomposition was determined by measuring the gas evolved. By plotting temperatures as abscissæ and volumes of (1) nitrogen and (2) ammonia disengaged as ordinates, two curves were obtained cutting one another on the temperature axis, and thus giving the temperature of decomposition, which is sometimes 50° below that actually observed subjectively. When the evolution of gas ceases, the contents of the tubes were distilled, and give as a rule (1) a mixture of aldazine and the stilbene; (2) green oils containing the phenanthrene; (3) red oils, and (4) a resinous or coke-like residue. In the case of the "red oils" from benzaldazine the chief constituent is a substance, m. p. 261°, b. p. 460°, crystallising in long needles and giving a yellow picrate, m. p. 198°; it may be identical with the product $C_{28}H_{23}N_3$ obtained by Curtius from benzoin-hydrazine. The amounts of this substance and its homologues produced increase with rise in the molecular weight of the aldazine employed.

Benzaldazine, $CHPh:N_2:CHPh$, begins to decompose at 275°, furnishing stilbene, phenanthrene, and the product $C_{28}H_{23}N_3$ already referred to. Tolualdazine, $C_6H_4Me:N_2:C_6H_4Me$, begins to decompose at 314°, forming di-*p*-methylstilbene, m. p. 181°. *Cuminaldazine*,

$$C_6H_4Pr^{\beta}\cdot CH:N_2:CH\cdot C_6H_4Pr^{\beta},$$

m. p. 113·6°, forms yellow leaflets, and begins to decompose at 281°, yielding *di*-p-iso*propylstilbene*, $C_6H_4Pr^{\beta}\cdot CH:CH\cdot C_6H_4Pr^{\beta}$, m. p. 129°, which separates from alcohol in colourless scales, and yields a *dibromide*, m. p. 186—187° (approx., decomp.), crystallising in small, brilliant, colourless spangles.

p-*Methylbenzaldazine*, $CHPh:N_2:CH\cdot C_6H_4Me$, m. p. 112°, forms pale yellow crystals from alcohol, and when heated gives *p*-methylstilbene m. p. 119·6°. Aldazines in which the benzene nucleus is replaced by naphthalene decompose only at high temperatures, and the unsaturated product is difficult to free from tarry by-products. Furfuraldazine, $C_4OH_4\cdot CH:N_2:CH\cdot C_4OH_4$, is decomposed by heat, yielding furfurylstilbene, m. p. 97·4°.

The aliphatic azines of low molecular weight distil easily, and decompose only at a red heat. The higher terms decompose slowly on distillation, forming a fluorescent liquid with an odour of petroleum and of pyridine bases; there is no evolution of nitrogen or ammonia.

Di-p-*chlorobenzaldazine*, m. p. 211°, forms yellow spangles from alcohol or boiling benzene; it begins to decompose at 284°, furnishing *di*-p-*chlorostilbene*, m. p. 153·8°, in silver-grey spangles, which yields a *dibromide*, m. p. 195—197°. *Di*-p-*iminobenzaldazine*, m. p. 245°, obtained by the interaction of *p*-aminobenzaldehyde with hydrazine sulphate, is a yellow powder; it begins to decompose at 307°, giving off a little nitrogen and much ammonia, so that it was impossible to isolate di-*p*-aminostilbene from the accompanying tarry by-products.

Di-*o*-methoxybenzaldazine begins to decompose at 270°, and yields 80% of di-*o*-methoxystilbene, m. p. 136°, which separates from alcohol in colourless crystals and gives a *dibromide*, m. p. 190°; the corresponding *meta*-compound furnishes di-*m*-methoxystilbene, m. p. 97·5°, the *dibromide* of which, m. p. 183·5—184·5°, is colourless and crystalline. Di-*p*-methoxybenzaldazine begins to decompose at 289°, and yields di-*p*-methoxystilbene, m. p. 213°. *Di*-o-*ethoxybenzaldazine*, m. p. 131·6°, forms yellow crystals, and commences to decompose at 287°, giving *di*-o-*ethoxystilbene*, m. p. 87·5°, colourless crystals, the *dibromide* of which, m. p. 218—219°, forms pale yellow crystals. *Di*-p-*ethoxybenzaldazine*, m. p. 172·3°, crystallises in pale yellow lamellæ, and begins to decompose at 308°, furnishing di-*p*-ethoxystilbene, m. p. 208°.

Di-o-*benzyloxybenzaldazine*, m. p. 157·7°, yellow plates, gives di-*o*-benzyloxystilbene, m. p. 117·6°, in small, brilliant, colourless spangles, whilst the corresponding para-compound, m. p. 209·3°, pale yellow leaflets, decomposes less easily, forming a bulky "coke" from which no stilbene derivative has yet been isolated. T. A. H.

Decomposition of Azines by Heat. III. Paul Pascal and Léon Normand (*Bull. Soc. chim.*, 1912, [iv], 11, 21—25. Compare preceding abstract).—The *methoxynaphthaldazine* gives only a small yield of dimethoxynaphthylethylene at 362°. *Veratraldazine* gives but little 3 : 4 : 3′ : 4′-tetramethoxystilbene, whilst the *azine* from piperonaldehyde, $N_2(:CH\cdot C_6H_3:O_2:CH_2)_2$, does not yield a corresponding stilbene. The main conclusions arrived at from results described in this and the preceding abstracts are as follows.

Aromatic azines decompose at about 300°, evolving nitrogen and ammonia, and giving stilbene derivatives, the yields being increased if the position ortho to the group $\cdot CH:N_2:$ is filled by any radicle. In the same homologous series the yield diminishes on ascending the series. If a substituent group, such as amino-, in the nucleus of the azine possesses a residual affinity, the yield of stilbene compound is considerably lowered. Esterification in the case of several hydroxy-groups attached to each aromatic nucleus does not prevent decomposition.

A study of the physical constants of the azines and stilbenes shows that the introduction of one or more atoms of oxygen into the molecule produces a rise in the melting point. The reverse is the case if a hydroxyl group is replaced by a methoxy- or ethoxy-group. Finally, the more symmetrical the molecule the higher is the melting point.

W. G.

The Existence of Sulphur Fixed as Sulphite in Wool. H. Strunk and Hans Priess (*Zeitsch. physiol. Chem.*, 1912, 76, 136—144).—Raikow (Abstr., 1905, i, 725; 1907, i, 666; compare Grandmougin, *Chem. Zeit.*, 1907, 31, 174) has stated that wool, when kept for some time in contact with large quantities of concentrated phosphoric acid, liberates small quantities of sulphurous acid. This is confirmed, but the amount, 0·0064 gram of sulphur dioxide from 300 grams of wool, is too small for it to be assumed that part of the

sulphur in the keratin molecule is united with oxygen as sulphite. Dry wool has a very pronounced affinity for hydrogen sulphide; this is sufficient to explain the variations experienced in the amount of sulphur in wool. The hydrogen sulphide fixed by the wool is easily oxidised to sulphurous and sulphuric acids, and it is probable that a small quantity of sulphurous acid may arise in the wool of the living animal in such manner. E. F. A.

The Separation of Rennet and Pepsin. W. E. BURGE (*Amer. J. Physiol.*, 1912, **29**, 330—334).—The passage of a direct current of 10 milliamperes for twenty-four hours through a solution containing both enzymes causes a complete destruction of peptic activity, but leaves the rennet apparently unchanged. W. D. H.

Activation of Sucrase [Invertase] by Different Acids. GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Compt. rend.*, 1912, **154**, 1515—1518).—The effect of the more common organic and inorganic acids on the diastatic activity of sucrase has been determined under conditions more precisely defined than those of other observers. In each case the optimum concentration of acid was determined. The results, which are displayed in tabular form, show that, generally speaking, the order of efficiency in which the acids stand as activating agents is the same as Ostwald's order for their activity as catalysts in hydrolysis. Hydrochloric and nitric acids, however, are exceptions to the rule, being less effective as activators than as catalysts. W. O. W.

Action of Phosphatese. HANS EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1912, **76**, 241. Compare Abstr., 1911, i, 1051; this vol., i, 61).—Reference is made to von Lebedeff's work, which does not agree with that of the authors; perhaps different kinds of yeast will explain the discrepancy; no further experimental work is adduced. W. D. H.

4-Amino-3-hydroxyphenylarsinic Acid and its Products of Reduction. LUDWIG BENDA (*Ber.*, 1911, **44**, 3578—3582. Compare this vol., i, 61—64).—3-Nitro-4-aminophenylarsinic acid can be diazotised in the usual way, yielding a solution of a diazonium salt, which loses the $\cdot AsO(OH)_2$ group when boiled with dilute sulphuric acid. However, by treatment with sodium acetate to destroy the mineral acid, the solution of the diazonium salt exchanges its nitro- for a hydroxyl group; the solution of the resulting diazonium salt can be coupled with alkaline β-naphthol to form a red azo-dye, which is reduced by sodium hyposulphite or by sodium hydroxide and aluminium, yielding 1-amino-2-naphthol and 4-*amino-3-hydroxyphenylarsinic acid*, $NH_2\cdot C_6H_3(OH)\cdot AsO(OH)_2$, the *sodium* salt, $C_6H_7O_4NAsNa,5H_2O$, and *silver* salt of which are described.

Under suitable conditions, the red azo-dye is reduced by sodium hyposulphite, yielding 4 : 4′ - *diamino* - 3 : 3′ - *dihydroxyarsenobenzene*, $As_2[C_6H_3(NH_2)\cdot OH]_2$, the *hydrochloride* and *sulphate* of which are described. C. S.

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Organic Chemistry.

Catalysis and the Formation of Petroleum. CARL ENGLER and E. SEVERIN (*Zeitsch. angew. Chem.*, 1912, 25, 153—158).—Repetition of Künkler's experiments on the distillation of crude oleic and stearic acids at atmospheric pressure (*Chem. Zentr.*, 1910, i, 2031) shows that decomposition begins at 340° and 358° respectively, and that the formation of hydrocarbons is small and commences at about 400°. The suggestion of Künkler and Schwedhelm (Abstr., 1909, i, 281) that soaps may first be formed by the interaction of lime or alumina with fats, and that these under the influence of heat may give rise first to ketones, and eventually to the hydrocarbons of petroleum, is untenable, since ketones have not been found either in bitumens or petroleum, and no indication of the existence of soaps in bitumen could be found by the authors. Various investigators have suggested that rock-forming materials by their action on organic remains may play some part in the formation of petroleum, and some support to this view is afforded by the work of Sabatier, Senderens, and Mailhe on the catalytic decomposition of aliphatic acids and their esters by metallic oxides (compare Ipatieff, Abstr., 1904, ii, 644, 645; 1911, i, 937), and Gräfe (*Petroleum*, 1910, 6, 71) has pointed out that *Lycopodium* spores distilled with fuller's earth afford a distillate similar in character to Scottish shale oil. The authors have therefore examined the distillates obtained from mixtures of oleic or stearic acid with diatomite, fuller's earth, quartz sand, and finely powdered quartz, and find that these materials lower the temperature of decomposition and give rise to distillates richer in hydrocarbons than are obtained when the acids are distilled alone. Powdered quartz is the most efficient of the four, followed by fuller's earth, which is better than either diatomite or sand (compare Hviid, *Petroleum*, 1910, 6, 429). The distillates, full details of which are given in the original, in general resemble those obtained by distillation of fatty acids under pressure (Abstr., 1888, 928), but contain more undecomposed acid and less low-boiling hydrocarbons. The conclusion is drawn that in the conversion of organic remains into petroleum, the influence of rock-forming materials as well as of time, temperature, and pressure must be taken into account. T. A. H.

Presence of Cholesterol in Java Naphthas. CARL ENGLER and WILHELM STEINKOPF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1820—1825).—The work of Koss (Abstr., 1911, i, 761), which was carried out partly under the supervision of the authors, and also its unauthorised publication are severely criticised. T. H. P.

Valency of Carbon in So-called Unsaturated Compounds. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1690—1735).—A discussion of the various explanations which have

been advanced of the unsaturated character of the carbon atom in different classes of organic compounds. T. H. P.

$\beta\beta\gamma$-Trimethylpentane. LATHAM CLARKE and WEBSTER NEWTON JONES (*J. Amer. Chem. Soc.*, 1912, **34**, 170—174).—In continuation of a study of the octanes (Abstr., 1911, i, 354, and earlier abstracts), $\beta\beta\gamma$-trimethylpentane has now been synthesised. By the action of magnesium ethyl bromide on pinacolin, $\beta\beta\gamma$-trimethylpentan-γ-ol was produced, and was converted into γ-iodo-$\beta\beta\gamma$-trimethylpentane by the action of iodine and amorphous phosphorus. On treating this carbinyl iodide with alcoholic potassium hydroxide, $\beta\beta$-dimethyl-γ-methylenepentane was obtained, and on passing this over finely divided nickel at 160° in a current of hydrogen, $\beta\beta\gamma$-trimethylpentane was produced.

$\beta\beta\gamma$-Trimethylpentan-γ-ol, $CMe_3{\cdot}CMe(OH){\cdot}CH_2Me$, b. p. 149—152°/760 mm., is a colourless liquid with a camphor-like odour. The *octylene* (*$\beta\beta$-dimethyl-γ-methylenepentane*), $CMe_3{\cdot}C(:CH_2){\cdot}CH_2Me$, b. p. 110·4—110·8°/760 mm., is a colourless, mobile liquid with a faint, musty odour. *$\beta\beta\gamma$-Trimethylpentane*, $CMe_3{\cdot}CHMe{\cdot}CH_2Me$, b. p. 110·5—110·8°/760 mm., D_{15}^{15} 0·7219, n_D^{25} 1·4164, is a colourless, mobile liquid with a very faint odour. E. G.

$\beta\delta$-Dimethylheptane. LATHAM CLARKE and SYDNEY A. BEGGS (*J. Amer. Chem. Soc.*, 1912, **34**, 60—62).—In continuation of the work on the nonanes (following abstract), $\beta\delta$-dimethylheptane has been synthesised.

When β-methyl-δ-pentanone (methyl *iso*butyl ketone), obtained by the hydrolysis of ethyl *iso*propylacetoacetate, is treated with magnesium *n*-propyl iodide, the *nonylene* (*β-methyl-δ-methyleneheptane*),

$$CH_2Me{\cdot}CH_2{\cdot}C(:CH_2){\cdot}CH_2{\cdot}CHMe_2,$$

b. p. 132—133°, is obtained as a colourless liquid with an odour resembling that of petroleum. The position of the double bond was not established, but there is little doubt that the formula assigned to the compound is correct. On passing a mixture of the nonylene and hydrogen over freshly reduced nickel, *$\beta\delta$-dimethylheptane*,

$$CH_2Me{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CHMe_2,$$

b. p. 132·9—133°/752 mm., D_{15}^{15} 0·7206, n_D^{25} 1·4014, is produced as a colourless liquid with a petroleum-like odour. E. G.

$\beta\epsilon$-Dimethylheptane. LATHAM CLARKE and SYDNEY A. BEGGS (*J. Amer. Chem. Soc.*, 1912, **34**, 54—60).—In a study of the octanes (Abstr., 1911, i, 354, and earlier abstracts), certain relations have been discovered between the chemical constitution and physical properties. An investigation has been undertaken in order to ascertain whether similar relations occur in the nonane series, and an account is now given of the synthesis and properties of $\beta\epsilon$-dimethylheptane which has been obtained previously in an impure state by Welt (Abstr., 1896, i, 332).

The synthesis was effected in the following manner. β-Methyl-ϵ-hexanone, obtained by the hydrolysis of ethyl *iso*butylacetoacetate, was converted into $\beta\epsilon$-dimethyl-ϵ-heptanol by means of magnesium

ethyl bromide. The iodide of this alcohol was prepared, and when boiled with alcoholic potassium hydroxide yielded β-methyl-ϵ-methyleneheptane, which was then reduced to $\beta\epsilon$-dimethylheptane.

$\beta\epsilon$-Dimethyl-ϵ-heptanol, $CH_2Me\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CHMe_2$, b. p. 172—174°, is a colourless liquid with an odour of musty apples. The *nonylene* (*β-methyl-ϵ-methyleneheptane*),

$$CH_2Me\cdot C(\colon CH_2)\cdot CH_2\cdot CH_2\cdot CHMe_2,$$

b. p. 139—140°, is a colourless liquid with a sweet, petroleum-like odour. $\beta\epsilon$-Dimethylheptane, $CH_2Me\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe_2$, b. p. 135·6—135·9°/760 mm., D_{15}^{15} 0·7190, n_D^{25} 1·4020, obtained by passing a mixture of the nonylene and hydrogen over freshly reduced nickel at 160—180°, is a colourless liquid with a petroleum-like odour.

E. G.

Conjugated *aci*-Nitro-compounds. ARTHUR HANTZSCH and KURT VOIGT (*Ber.*, 1912, **45**, 85—117).—A number of nitro-compounds, chiefly aliphatic substances containing NO_2 attached to carbon, have been examined spectrometrically to determine how the absorption spectrum is affected when the real nitro-group is changed to an *aci*-nitro-group. The chief result of the investigation has been the discovery of a new type of nitro-compound, which is called a conjugated *aci*-nitro-compound.

The nitro-group may be present in a substance in three forms, each of which has its characteristic absorption curve. Aliphatic real nitro-compounds show very feeble selective absorption, the curves exhibiting a very flat band or a kink beginning at oscillation frequency 3413. It is immaterial whether the nitro-group is the only negative substituent in the molecule or whether another (NO_2, NOH, CO, CO_2H, CO_2Et, $CO\cdot NH_2$, CN, Ph) is present, provided that the introduction of the latter does not produce a constitutive change in the nitro-group. A simple *aci*-nitro-group, $>C\colon NO\cdot OH$, causes weak general absorption; such groups are present only in the salts of the nitroparaffins, $CHR\colon NO\cdot OM$. When, however, an *aci*-nitro-group is present together with another negative group, X (one of those mentioned above), then, without exception, the substance exhibits very strong, selective absorption, the curve exhibiting a very deep band for thicknesses corresponding with 10 to 100 mm. of *N*/10,000 solution. Since the introduction of a negative group into a real nitro-compound has little optical influence, whilst a simple *aci*-nitro-group alone causes general absorption, it follows that the strong selective absorption exhibited by a substance containing both an *aci*-nitro- and another negative group must be conditioned by the influence of these two groups on one another. This influence is represented by a peculiarly constituted, six-membered ring, produced by the union, by a supplementary valency, of a metallic or hydrogen atom, or of an alkyl group with a negative atom of the negative (unsaturated) group X: $R\cdot C{<}^{X\cdots}_{NO\cdot O}{>}(Na,H,Me)$. For examples, X is a nitro-group in *aci*-dinitro-compounds (salts of di- and tri-nitromethane), an $R\cdot CO$ group in α-*aci*-nitroketones (the nitrobarbituric acids; ethyl *aci*-nitromalonate), and a cyano-group in α-cyano-

aci-nitro-compounds (fulminuric esters; *aci*-nitrocyanophenylmethane). An *aci*-nitro-group in this state is called a conjugated *aci*-nitro-group. Its presence explains why the introduction of a third negative group into the molecule exerts so slight an optical influence; the third group can only have a feeble auxochromic effect. *aci*-Nitrophenylmethane and its salts contain a conjugated *aci*-nitro-group; consequently the benzene nucleus, by means of a supplementary valency (in the ortho- or para-position), can form part of the six-membered complex.

Certain conjugated *aci*-nitro-compounds (fulminuric acid and the nitrobarbituric acids) are so stable that they cannot be converted, even by concentrated sulphuric acid, into real nitro-compounds. Furthermore, substances containing a simple *aci*-nitro-group together with another unsaturated group are incapable of existence; therefore, when a real nitro-compound containing another unsaturated group is transformed into an *aci*-nitro-compound, a conjugated *aci*-nitro-group is always produced.

The chromoisomerism of certain conjugated *aci*-nitro-compounds, for example, the yellow and the colourless salts of the nitrobarbituric acids, cannot be explained by regarding the yellow salt as containing a conjugated *aci*-nitro-group and the colourless salt as containing a simple *aci*-nitro-group, because the latter group cannot exist in such compounds. Both salts contain the conjugated *aci*-nitro-group. The colour of the yellow salt is due to a shifting of the absorption band towards the red end of the spectrum. Chromoisomerism in such cases, therefore, is merely valency isomerism and is represented thus:

$$\begin{array}{l}\mathrm{-C{:}O\cdots M}\\ \quad| \qquad\quad \vdots\\ \mathrm{-C{:}NO{\cdot}O}\end{array} \quad\text{and}\quad \begin{array}{l}\mathrm{-C{\cdot}O{-}M}\\ \quad\| \qquad\quad \vdots\\ \mathrm{-C{\cdot}NO{:}O}\end{array}.$$

When the ionisation of a substance containing a conjugated *aci*-nitro-group is unaccompanied by secondary changes, the ions are optically identical with the undissociated acid, and therefore contain the peculiar six-membered ring. This result leads to Werner's theory that the formation of ions is, in the first step, a case of hydrate formation. For the particular examples under discussion, the ionisation is represented by the scheme:

$$\mathrm{R{\cdot}C}\Big\langle\begin{array}{c}\mathrm{-\!-X-\!-}\\ \mathrm{NO{\cdot}O}\end{array}\Big\rangle\mathrm{H} \rightarrow \mathrm{R{\cdot}C}\Big\langle\begin{array}{c}\mathrm{-\!-X\cdots}\\ \mathrm{NO{\cdot}O}\end{array}\Big\rangle\mathrm{H\cdots OH_2} \rightarrow$$

$$\mathrm{R{\cdot}C}\Big\langle\begin{array}{c}\mathrm{-\!-X-\!-}\\ \mathrm{NO{\cdot}O}\end{array}\Big\rangle\mathrm{H_2O' + H^{\cdot}}.$$

In conclusion, attention is drawn to the extensive optical and chemical analogies between negatively substituted nitro-compounds on the one hand, and negatively substituted ketones (ethyl acetoacetate) on the other.

C. S.

Aliphatic Nitro-compounds. XII. Constitution of *aci*-Nitro-compounds. WILHELM STEINKOPF and BORIS JÜRGENS (*J. pr. Chem.*, 1911, [ii], 84, 686—713. Compare Abstr., 1911, i, 530).—The formation of hydroxamic chlorides by the action of hydrogen chloride on aliphatic nitro-compounds is referred by the authors to the decomposition of the *aci*-nitro-compound into the corresponding aldehyde and nitroxyl, which then combine to form a nitroso-alcohol (I); the latter compound reacts with hydrogen chloride, yielding a chloronitroso-

compound (II), which then undergoes transformation into the hydroxamic chloride (III), as shown in the following scheme:

R·CH:NO·OH ⟶ R·CHO + :NOH ⟶ (I) R·CH(NO)·OH ⟶
(II) R·CHCl·NO ⟶ (III) R·CCl:N·OH.

This view is supported (1) by the observations of Nef (Abstr., 1895, i, 3), and also of Hantzsch and Veit (Abstr., 1899, i, 401), who find that *aci*-nitro-derivatives of hydrocarbons readily decompose into aldehyde, nitrous oxide, and water; (2) by the formation of hydroxamic acids by the direct combination of aldehydes and nitroxyl (Angeli), and (3) by the production of blue or green colorations, due to the formation of chloronitroso-compounds, R·CHCl·NO, when salts of the nitro-derivatives of aliphatic hydrocarbons are acidified in aqueous or ethereal solution. Attempts have been made to isolate these coloured compounds in the case of nitromethane, nitropropane, and nitroethane, but only with the last-mentioned compound were the attempts successful. When a suspension of the sodium salt of *aci*-nitroethane in a large volume of ether is treated with an excess of hydrogen chloride, and the resulting solution, after removal of the sodium chloride, rapidly evaporated, chloronitrosoethane (Piloty and Steinbock, Abstr., 1902, i, 735) was obtained. If a small volume of ether is used and excess of hydrogen chloride avoided, the product consists of ethylnitrolic acid. The formation of the latter compound is due to the action of nitrous acid, produced by the decomposition of the intermediately formed nitroso-alcohol, NO·CMeH·OH, on unchanged nitroethane.

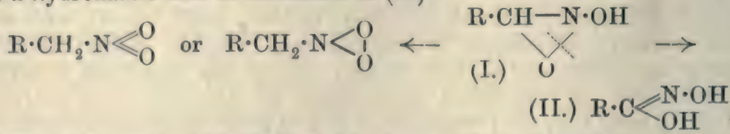
Salts of nitro-compounds, such as nitroacetic acid and nitroacetonitrile, which contain strongly negative groups do not give blue or green colorations when treated with acids, and the conclusion is therefore drawn that in these cases decomposition of the *aci*-nitro-compound into aldehyde and nitroxyl does not take place.

This view is supported by the behaviour of ω-nitroacetophenone, which on treatment with hydrogen chloride in ethereal solution yields ω-chloro-ω-oximinoacetophenone (Thiele and Haeckel, Abstr., 1903, i, 160), without the intermediate formation of a coloured nitroso-compound. *aci*-Phenylnitromethane, which contains the feebly negative phenyl group, occupies an intermediate position; with ethereal hydrogen chloride, it develops the blue coloration very slowly, instead of instantly as in the case of the nitro-derivatives of aliphatic hydrocarbons, and this coloration gradually disappears owing to the formation of benzhydroxamic acid.

These differences in the behaviour of nitro-compounds are best explained on the assumption that the *aci*-nitro-derivative has the constitution, CRH—N·OH, proposed by Hantzsch, and not the
\\ /
O
Michael-Nef formula, CHR:NO·OH, now generally accepted. The stability of the carbazoxy-ring depends on the nature of the substituents. When R = H or alkyl, the ring is unstable, and readily suffers complete rupture, as indicated in the following scheme:

R·CH-¦-N·OH
\\ / ⟶ R·CHO + :N·OH.
O

On the other hand, when R is a strongly negative group, the stability of the ring is greatly increased, so that rupture occurs only at one point, either between C and O, with the formation of a nitro-compound as shown in (I) below, or between N and O, with the formation of a hydroxamic acid as indicated in (II):



The evidence furnished by Nef in favour of the formula

R·CH:NO·OH

for *aci*-nitro-compounds is subjected to a critical examination, and the conclusion is drawn that Hantzsch's formula affords a simpler and less forced explanation of the behaviour of these compounds.

Numerous examples of the reactions of nitro-compounds and of a large number of other classes of compounds containing the carbazoxy-ring are cited in support of the authors' view. F. B.

Specific Gravity Table of Alcohol–Water Mixtures at 17·5°. WILHELM FRESENIUS and LEO GRÜNHUT (*Zeitsch. anal. Chem.*, 1912, 51, 123—124).—A useful table giving $D_4^{17\cdot5}$ for a number of mixtures of alcohol and water, together with the corresponding alcohol % by weight and by volume, and also alcohol in grams per 100 c.c. L. DE K.

Action of Potassium Hydroxide on Secondary Alcohols; Diagnosis of Primary and Secondary Alcohols of High Molecular Weight. MARCEL GUERBET (*Compt. rend.*, 1912, 154, 222—225. Compare this vol., i, 67).—When secondary alcohols are heated at 230° with potassium hydroxide, some oxidation occurs with production of potassium salts of acids, but the greater part of the alcohol forms condensation products; thus *iso*propyl alcohol yields formic and acetic acid, together with β-methylpentan-δ-ol and βδ-dimethylheptan-ζ-ol. The corresponding higher homologues are obtained from *sec.*-butyl alcohol and octyl alcohol. The ease with which the reaction is carried out renders it suitable for distinguishing between secondary and primary alcohols. W. O. W.

Specific Gravity and Hygroscopic Power of Glycerol. ANTON KAILAN (*Zeitsch. anal. Chem.*, 1912, 51, 81—101).—Anhydrous glycerol has D_4^{15} 1·26413. The density between 14° and 20° can be calculated by the expression $D_4^t = 1\cdot26413 + (15 - t)\ 0\cdot000632$, and a table is given of densities from 14·3° to 20·6°. Boiling points under various pressures between 9 and 32 mm. are also recorded.

Glycerol rapidly absorbs moisture from the air, and a number of determinations of the hygroscopic power of anhydrous and hydrated samples are given. It appears that a mixture containing 80% of glycerol is in equilibrium with air containing an average amount of moisture.

The author also noticed that alcohol containing but little water absorbs, in the same circumstances, water four times more rapidly than does a similar glycerol. L. DE K.

Preparation of Epichlorohydrin from Dichlorohydrin and Alkalis. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 239077).—When dichlorohydrin (129 parts) in 200 parts of water is slowly treated with 133 parts of 30% sodium hydroxide solution, it yields 85 parts of epichlorohydrin; the sodium hydroxide may be replaced by its equivalent of potassium or ammonium hydroxide, but the above concentrations must be carefully maintained. F. M. G. M.

Tautomerism of the Dialkyl Phosphites. THADDEUS MILOBENDZKI (*Ber.*, 1912, **45**, 298—303).—Previous investigations (Abstr., 1897, i, 391; 1908, ii, 488; 1903, i, 733; 1907, i, 8, 1899, i, 659) have indicated that dialkyl hydrogen phosphite in the free condition has the constitution (I) $O:PH(OR)_2$. From the behaviour of the esters in aqueous solution, the author shows that they also exist in the tautomeric form (II) $OH\cdot P(OR)_2$.

Silver salts of the composition $Ag\cdot PO(OR)_2$ are precipitated from aqueous solutions of di*iso*propyl hydrogen phosphite (b. p. 74—75°/9 mm.) and diethyl hydrogen phosphite (b. p. 66—67°/9 mm.) by the successive addition of silver nitrate and aqueous alkalis (ammonia, sodium hydroxide, and barium hydroxide); the addition of the reagents in the reverse order produces no precipitate.

According to the author the silver salts, $OAg\cdot P(OR)_2$, are readily soluble in water, and the non-formation of a precipitate, when the alkali is added before the silver nitrate is due to the transformation of the keto-ester (I) into the enolic form (II).

The silver salts, $Ag\cdot PO(OR)_2$, dissolve in excess of alkali owing to change into the tautomeric form, induced by the hydroxyl ions; on acidifying the alkaline solutions, the original salt is precipitated.

Dialkyl hydrogen phosphites show the phenomenon of gradual neutralisation. The percentage of the ester (I) present in aqueous solutions has been determined by adding the equivalent amount of aqueous ammonia, followed immediately by the addition of silver nitrate; the amount of silver salt, $Ag\cdot PO(OR)_2$, precipitated corresponds with that of the ester of the formula (I) originally present; with diethyl hydrogen phosphate the amount is 35%.

That the enolic modifications of the esters are capable of existing in aqueous solution has also been shown by neutralising with aqueous barium hydroxide, and then adding the equivalent amount of sulphuric acid; the solutions thus obtained do not show the phenomenon of gradual neutralisation, nor yield insoluble silver salts.

Triethyl phosphite is hydrolysed by excess of aqueous sodium hydroxide to sodium diethyl hydrogen phosphite; dialkyl hydrogen phosphites are not hydrolysed by alkalis.

Experiments are also described showing that *sodium diethyl phosphite*, prepared from sodium and diethyl hydrogen phosphite in ethereal solution, exists in aqueous solution in the form $NaO\cdot P(OEt)_2$.

F. B.

Constitution of Glycerophosphoric Acid Prepared by Esterification of Phosphoric Acid or Sodium Dihydrogen Phosphate. PAUL CARRÉ (*Compt. rend.*, 1912, **154**, 220—222.* Compare Abstr., 1904, i, 133, 215).—Sodium glycerophosphate,

* and *Bull. Soc. chim.*, 1912, **11**, 169—172.

prepared by Poulenc's method, was converted into glycerophosphoric acid by the process previously described. The product is identical in every respect with the acid formed in the direct esterification of phosphoric acid by glycerol. The same acid is obtained when glycerol bromohydrin (3 mols.) is heated with silver phosphate and the resulting unstable *ester*, $OP[O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH]_3$, submitted to hydrolysis. Poulenc's compound must, therefore, be a salt of α-glycerophosphoric acid, and not of the β-acid as stated by Paolini (Abstr., 1911, ii, 774). The author has been unable to obtain Paolini's brucine salt crystallising with $7H_2O$. W. O. W.

Preparation of Glycol and Glycolhydrin Esters of Phosphoric Acid Glycerides. ADOLF GRÜN and FRITZ KADE (D.R.-P. 240075).—Compounds of general formula $X\cdot C_2H_4\cdot O\cdot PO(OH)\cdot O\cdot C_3H_5(O\cdot CO\cdot R)_2$, where R is an alkyl group and X halogen or hydroxyl, can be readily prepared by the action of phosphoric oxide on distearin and ethylene-glycol or halogenhydrins.

The following products are described: the *compound*,

$$C_2H_4Cl\cdot O\cdot PO(OH)\cdot O\cdot C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2,$$

m. p. 65—66°; the *compound*,

$$OH\cdot C_2H_4\cdot O\cdot PO(OH)\cdot O\cdot C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2,$$

from $\alpha\beta$-distearinphosphoric acid ester, ethylenechlorohydrin, and glycol. The *trimethylamine* salt,

$$C_2H_4Cl\cdot O\cdot PO(O\cdot NHMe_3)\cdot O\cdot C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2,$$

m. p. 69°; and by the interaction of another molecule of trimethylamine, the *salt*,

$$NMe_3Cl\cdot C_2H_4\cdot O\cdot PO(O\cdot NHMe_3)\cdot O\cdot C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2.$$

F. M. G. M.

The Agglutination of Lecithins and Lecithin-protein Mixtures by Acids. J. FEINSCHMIDT (*Biochem. Zeitsch.*, 1912, **38**, 244—251).—Aqueous suspensions of lecithins of various origins have agglutination optima at definite hydrogen ion concentrations, which are identical with the isoelectric point. This varies in the different preparations between 10^{-2} and 10^{-4}, that is, in somewhat strongly acid solutions. Neutral salts increase the turbidity of the solutions, but make the actual agglutination point less sharp. When lecithin and protein are mixed, a new complex is formed, in which the agglutination point shifts towards the less acid side; in this case the precipitation is more energetic and coarser. S. B. S.

Catalytic Decomposition of Formic Esters. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1912, **154**, 49—52. Compare Abstr., 1911, i, 258—416).—The catalytic decomposition of alkyl formates below 400° is somewhat complicated, and follows a different course from that of esters of higher acids. In general, two principal reactions occur, represented by the equations: (1) $2H\cdot CO_2R = H\cdot CHO + CO_2 + R_2O$, followed by the dehydration of the aldehyde with production of an unsaturated hydrocarbon; (2) $H\cdot CO_2R = CO + R\cdot OH$, followed by dehydration or dehydrogenation of the alcohol. The water set free may effect hydrolysis, the resulting formic acid then decomposing in the manner already described.

The nature of the catalyst considerably influences the course of reaction; thus in the case of methyl formate and titanium oxide, reaction (1) predominates, whilst with zinc oxide reaction (2) occurs almost exclusively. Both reactions take place with thorium dioxide. Finely divided platinum, nickel, and copper readily effect catalysis, principally in accordance with equation (2). W. O. W.

Catalytic Formation of Saturated Aliphatic Esters from Formic Esters. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1912, **154**, 175—177. Compare preceding abstract).—When the vapour of methyl formate and *iso*butyric acid in equimolecular proportions is passed over titanium oxide at 250°, carbon monoxide is liberated, and the condensed liquid contains 20% of methyl *iso*butyrate, together with methyl alcohol and some *iso*butaldehyde. The esterification is explained by the decomposition of the methyl formate in the manner previously described, whilst the aldehyde arises from reduction of the acid by formic acid. Thorium oxide acts in the same way, but requires a higher temperature; thus at 300—330°, *iso*valeric acid and methyl formate give 40% of methyl *iso*valerate by volume and 16% of *iso*valeraldehyde. Under these conditions the amount of ketone formed is inconsiderable, but at 370° the condensed liquid contains 50% of ester, 10% of *iso*valerone, 15% of *iso*valeraldehyde, and also methyl alcohol.

Similar results have been obtained with higher acids and other alkyl formates. The direct reduction of acids by means of formic acid will be described in a further communication. W. O. W.

Optically Active Dialkylacetic Acids. EMIL FISCHER, JULIUS HOLZAPFEL, and HANS VON GWINNER (*Ber.*, 1912, **45**, 247—257. Compare Fischer and Flatau, Abstr., 1909, i, 628).—*a*-*iso*Butylhexoic acid has been resolved into optically active components by crystallisation of the brucine salt. The difference between the butyl and *iso*butyl radicles is apparently enough to cause pronounced optical asymmetry. *a*-*iso*Butylvaleric acid has also been resolved, but definite results were not obtained with *a*-*iso*propylvaleric acid.

*Ethyl butyl*iso*butylmalonate*, prepared by the interaction of *n*-butyl bromide on ethyl *iso*butylmalonate and sodium, has b. p. 137—140°/10 mm. When hydrolysed by means of sodium hydroxide, *butyl* iso*butylmalonic acid* is obtained in colourless crystals, m. p. 136—138°. The neutral solution of the ammonium salt gives a colourless precipitate with silver nitrate, and crystalline precipitates of the corresponding salts with barium and calcium chlorides. On heating at 160°, *butyl*iso*butylacetic* [*a*-iso*butylhexoic*] *acid* is obtained as a colourless oil, b. p. 145—145·5° (corr.)/10 mm. The *brucine* salt forms small, microscopic prisms. The first separations were hydrolysed by heating with sulphuric acid. The optically active *d*-*a*-*iso*butylhexoic acid had $[\alpha]_D^{22}$ +5·73°.

*Ethyl propyl*iso*butylmalonate* was obtained as an oil, b. p. 126°/9·5 mm.

Propylisobutylmalonic acid crystallises in stunted prisms or plates, m. p. 147—149° (corr., decomp.).

Propylisobutylacetic [*a-isobutylvaleric*] *acid* is a colourless oil, D^{20} 0·8928, b. p. 122° (corr.)/8·5 mm.; it forms a colourless *silver* salt, crystallising from ammonia in microscopic, slender needles. The *calcium* salt also consists of microscopic, slender needles. The *brucine* salt forms microscopic, small prisms, and yields *d-a-isobutylvaleric acid* as a colourless oil, m. p. 100°/0·5 mm., D^{22} 0·8876, $[\alpha]_D^{20}$ +9·8°.

The *monoamide* of *propylisopropylmalonic acid*,

$$CO_2H\cdot CPr^{\alpha}Pr^{\beta}\cdot CO\cdot NH_2,$$

obtained by heating cyano*iso*propylvaleric acid with concentrated sulphuric acid, crystallises in colourless bunches of intergrown prisms, m. p. 137° (corr., decomp.). When heated over the flame in a distillation flask, *a-isopropylvaleramide* is obtained at about 250°. It crystallises in slender, colourless needles, m. p. 131—133° (corr.).

By the action of sulphuric acid and sodium nitrite at 80°, *propylisopropylacetic* [*a-isopropylvaleric*] *acid* is obtained, b. p. 116° (corr.)/12 mm., 112—113°/9 mm., D^{17} 0·9076.

A partial resolution was obtained by means of the quinidine salt, the acid formed having $[\alpha]_D^{22}$ +0·77°. E. F. A.

Composition of Linseed Oil and the Distribution of Oxygen in Dried Layers of the Oil. II. E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1509—1524. Compare Abstr., 1910, i, 810).—The author criticises Fokin's work (Abstr., 1907, i, 820), the results of his own experiments being in agreement with Genthe's theory (*Zeitsch. angew. Chem.*, 1906, **19**, 2087), except that he finds that when a layer of the oil, 100—108 sq. cm. in area, weighs 0·1—0·15 gram, 15—16% of oxygen is taken up, although setting occurs when only 12% has been absorbed.

Experiments in which a cobalt dryer was employed give for the rates at which oxygen is fixed results corresponding with the formula $dx/dt = k(A-x)(B+x)$ or $k = \frac{1}{t(A+B)}\cdot\log\left(\frac{A}{A-x}\cdot\frac{B+x}{B}\right)$, where A represents the total amount of oxygen absorbed expressed as reduction of pressure, x the atmospheric pressure, and B a constant. After the oil has combined with 12% of its weight of oxygen, a solid phase is formed, and the further velocity of the absorbing process is expressed by $dx/dt = k(A-fx)(B+fx)$, where f, the correction coefficient, is less than unity, and corresponds with the product of combination of the solid phase, kf being a constant magnitude.

In parallel with this chemical process proceeds a physical one of diffusion of the oxygen into the oil, the amounts of oxygen in successive layers, starting from the surface, being in the proportions of $n, n^2, n^3, n^4 \ldots n^p$, where n is less than 1 (0·5, 0·6, etc.). The quantity of oxygen combined is related to the factor n, according to the expression $S/Q = n/(1-n)$, where Q is the quantity of combined oxygen corresponding with the iodine number, and S is the amount of oxygen found in each separate case. Assuming complete distribution

of the oxygen by diffusion, the value of n must be taken as two-thirds.
T. H. P.

Molecular Rearrangements in the Camphor Series. IX. Lauronolic Acid and Campholactone. WILLIAM A. NOYES and CHARLES E. BURKE (*J. Amer. Chem. Soc.*, 1912, 34, 174—183).—Tiemann (Abstr., 1901, i, 6) found that lauronolic acid prepared from bromocamphoric anhydride has a rotatory power which differs considerably from that of the acid obtained by the distillation of camphanic acid, and suggested that the acid produced by the latter method consisted of a mixture of optical isomerides. This has now been proved to be the case.

Lauronolic acid, prepared from active bromocamphoric anhydride by Aschan's method (Abstr., 1895, i, 154), has been obtained in the form of rosettes of long needles; it has m. p. 6·5—8°, b. p. 230—235° under the ordinary pressure, vapour pressure 99—100 mm. at 184°, $D_4^{27·5}$ 1·0109, D_4^{25} 1·0133, D_4^{10} 1·0249, $[\alpha]_D^{25}$ +187·7°, n_D 1·47586, and the dissociation constant K $1·36 \times 10^{-5}$. The calcium salt crystallises with $3H_2O$, instead of only $2H_2O$ as stated by Bredt (Abstr., 1911, i, 417), and when heated with soda-lime yields laurolene.

When hydrogen iodide is passed into a solution of lauronolic acid in light petroleum, the *hydriodide* is obtained in the form of yellow plates, and is very unstable. On reducing this compound with zinc dust and alcohol, *dihydrolauronolic acid*, $C_8H_{15}·CO_2H$, is produced, which has $D_4^{23·5}$ 0·9008, $[\alpha]_D^{25·5}$ +1·74°, vapour pressure 100 mm. at 178° and 749 mm. at 215°, and $[n]_D$ 1·45786; the *amide* has m. p. 50—51°.

By decomposing inactive bromocamphoric anhydride prepared from synthetical camphor, inactive lauronolic and camphanic acids were obtained. Inactive lauronolic acid has m. p. 5—8·5°, vapour pressure 100 mm. at 192°, D_4^{25} 1·0318, and $[n]_D$ 1·47655; its *calcium* salt crystallises with $1H_2O$.

Campholactone, prepared in various ways from lauronolic acids of widely different rotatory powers, has m. p. 50° and $[\alpha]_D^{22}$ −21·7°, and when warmed with barium hydroxide solution is converted into the corresponding hydroxy-acid, m. p. 143° and $[\alpha]_D^{27}$ +16·0°. E. G.

Molecular Rearrangements in the Camphor Series. VIII. Camphonolic Acid and Camphonololactone. WILLIAM A. NOYES, E. E. GORSLINE, and R. S. POTTER (*J. Amer. Chem. Soc.*, 1912, 34, 62—67).—Four hydroxy-acids and three lactones have been described which retain the tertiary carboxyl group of camphoric acid. The structural formulæ assigned to these compounds have not been well established, and the present work was therefore undertaken with the object of obtaining further evidence as to their constitution.

Camphononic acid, prepared by a modification of Lapworth and Lenton's method (Trans., 1901, 79, 1287), has m. p. 229—230°, $[\alpha]_D^{27·5}$ in benzene (2·4 grams in 100 c.c.) +17·8°, $[\alpha]_D^{28}$ in alcohol (2 grams in 100 c.c.) −3·9°. On reducing this acid with sodium and amyl

alcohol, *amyl camphonolate* is obtained as a yellow, viscous oil of b. p. 222—223°/40 mm.; the *calcium, copper*, and *silver* salts were prepared.

It is shown that the lactone obtained by Noyes and Taveau (Abstr., 1906, i, 397) by decomposing the nitroso-derivative of aminolauronic anhydride with sodium hydroxide is identical with *cis*-camphonololactone (annexed formula) prepared by Bredt (Abstr., 1909, i, 498) by the electrolytic reduction of camphononic acid. *cis*-Camphonololactone has m. p. 165—167°, $[\alpha]_D^{28}$ in alcohol (5 grams in 100 c.c.) $-20{\cdot}2°$ and $[\alpha]_D^{26}$ (10 grams in 100 c.c.) $-22{\cdot}3°$. The corresponding hydroxy-acid, *cis*-camphonolic acid (annexed formula), has m. p. 202—203° when rapidly heated, $[\alpha]_D^{28}$ in alcohol (10 grams in 100 c.c.) $+29{\cdot}2°$, and on oxidation with chromic acid is converted into camphononic acid. E. G.

$$\begin{array}{l} CH_2{\cdot}CMe{\cdot}CO \\ \quad\quad CMe_2 \\ CH_2{\cdot}CH{-}O \end{array} \qquad \begin{array}{l} CH_2{\cdot}CMe{\cdot}CO_2H \\ \quad\quad CMe_2 \\ CH_2{\cdot}CH(OH) \end{array}$$

The Melting Point of Oxalic Acid. EYVIND BÖDTKER (*Chem. Zeit.*, 1912, 36, 105).—Pure crystallised oxalic acid does not appear to have a definite melting point; a small crystal placed in a capillary tube had m. p. 99·5—101·5°, whilst a layer in the capillary tube, 1 mm. in height, had m. p. 100—102·5° when the temperature was raised very slowly and maintained at 100° for about one minute.

W. P. S.

Conversion of Maleic into Fumaric Acid. SEBASTIAN M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1742—1746).—It was discovered by Skraup (Abstr., 1891, 1338) that the interaction of hydrogen sulphide and sulphur dioxide in aqueous solution in presence of maleic acid is accompanied by transformation of the latter acid into fumaric acid; this effect he termed "resonance."

Since the reaction liquid, after filtration from the sulphur formed, contains nothing capable of bringing about this transformation, the author has investigated the action of sulphur on maleic acid. Milk of sulphur is without effect, and the same is apparently the case with the sulphur separated by the action of hydrogen sulphide on ferric chloride in presence of maleic acid. With sodium thiosulphate and a mineral acid, however, which normally give precipitation of sulphur, maleic acid prevents such precipitation and is simultaneously converted into fumaric acid; a similar transformation is produced, also without separation of sulphur, by addition of the thiosulphate to a solution of maleic acid alone. That these solutions contain no dissolved sulphur is shown by extraction with carbon disulphide, and the conclusion is drawn that it is the reaction of the thiosulphuric and maleic acids, with formation of an unknown product, that induces the isomeric change.

This same change is brought about by treatment of maleic acid with ammonia or potassium polysulphide (liver of sulphur), although in the latter case it may be due to the presence of thiosulphate.

T. H. P.

Relation between the Configuration and Rotation of the Lactones in the Sugar and Saccharinic Acid Groups. ERNEST ANDERSON (*J. Amer. Chem. Soc.*, 1912, **34**, 51—54).—Hudson (Abstr., 1910, i, 220) has pointed out that dextrorotatory sugar lactones have the ring on one side of the structure, whilst lævorotatory lactones have it on the other.

It is now shown that this relation is true, not only for the lactones to which Hudson referred, but for nearly all monobasic and some dibasic acid lactones in the sugar and saccharinic acid groups. The configurations and specific rotations of eighteen such lactones are tabulated. The relation affords a new method for determining the configuration of the lactones formed by certain dibasic acids.

E. G.

Ethyl Orthotrithioformate. BROR HOLMBERG (*Ber.*, 1912, **45**, 364—365).—In reply to Houben and Schultze (this vol., i, 5) it is claimed that the product obtained by the author (Abstr., 1907, i, 474) was pure. D. F. T.

Action of Potassium Hydroxide on Tetrolacetal. PAUL L. VIGUIER (*Compt. rend.*, 1912, **154**, 217—220. Compare Abstr., 1909, i, 691; this vol., i, 7).—When tetrolacetal (diethoxybutinene) is dropped on potassium hydroxide at 180—200°, a liquid distils, and on fractionation yields a *compound*, C_6H_8O, b. p. 29—33°/16 mm., $D^{19\cdot5}$ 0·826, $n_D^{19\cdot5}$ 1·462. This probably has the constitution

CH⋮C·CH⁚CH·OEt,

since it forms an explosive *silver* derivative, C_6H_7OAg, and is hydrolysed by acids, forming an unstable substance having the properties of the *aldehyde*, CH⋮C·CH_2·CHO. The latter changes spontaneously into triacetylbenzene, acetoacetaldehyde probably being produced first. Hydroxylamine yields 1-methyl*iso*oxazole. On treating the aldehyde with semicarbazide hydrochloride, a *semicarbazone*, $C_5H_8ON_3Cl$, is obtained; this yields the corresponding *aldehyde*, C_4H_5OCl, on hydrolysis. W. O. W.

Tartardialdehyde. ALFRED WOHL and BRUNO MYLO (*Ber.*, 1912, **45**, 322—349).—From the result of their endeavours, the authors conclude that the synthesis of tartardialdehyde by the symmetrical linking together of two molecules each containing two carbon atoms presents excessive difficulties, and they have finally attained success by other means.

The action on acetyl chloride of copper hydride gives ethyl acetate and ethylidene diacetate, whilst the action of copper on the additive product of dibromoacetaldehyde and acetyl bromide yields bromovinyl acetate. Dibromoacetaldehyde also reacts slowly with magnesium methoxide, the product being a $\beta\beta\delta$(or $\delta\delta\beta$-)-*tribromo-γ-keto-n-butyl alcohol*, b. p. 77—79°/14—16 mm.

Glyoxal sodium bisulphite in acetic anhydride solution reacts with hydrogen chloride producing unstable *s*-dichloroglycol diacetate, b. p. 110—115°/14 mm. (compare Prud'homme, *Zeit. Chem.*, 1870, 380).

Ethyl diethoxyacetate in ethereal solution with potassium gives as chief product an undistillable syrupy substance, *β-hydroxy-γ-ketosuccindialdehyde diethylacetal*, $CH(OEt)_2·CO·CH(OH)·CH(OEt)_2$; the substance was not obtainable in a pure state, and the action of sodium gave still less satisfactory results. The action of sodium on the piperidide of diethoxyacetic acid (Wohl and Lange, Abstr., 1908, i, 943) yields *monoethoxyacetopiperidide*, b. p. 72—74°/0·08—0·11 mm. *Diethoxyacetohydrazide*, obtained from the ethyl ester with hydrazine in alcoholic solution, forms capillary crystals, m. p. 43—45°, and has b. p. 110°/0·05 mm.; it reacts with mercuric oxide or metaboric acid, eliminating nitrogen and forming *bis-diethoxyacetohydrazide*,

$$CH(OEt)_2·CO·NH·NH·CO·CH(OEt)_2,$$

which crystallises in needles, m. p. 67—70°; the mercury, copper, and lead compounds are described. Iodine removes mercury from the mercury compound with the formation of *azo-α-ketodi-β-ethoxyethane*, $CH(OEt)_2·CO·N{:}N·CO·CH(OEt)_2$, a viscous, colourless oil, b. p. 131—134°/0·07—0·08 mm., which on warming decomposes, giving ethyl orthoformate, instead of the desired tetraethoxydiacetyl,

$$CH(OEt)_2·CO·CO·CH(OEt)_2.$$

Success was attained by starting with di-magnesium acetylene dibromide (from acetylene and magnesium ethyl bromide), which on treatment with ethyl orthoformate gives acetylenedialdehyde diethylacetal, $CH(OEt)_2·C{:}C·CH(OEt)_2$, $D^{18·5}$ 0·955 (compare Jotsitch, *Chem. Zeit.*, 1907, 31, 979); by reduction with hydrogen in the presence of colloidal palladium, this passes into *maleinaldehyde diethylacetal*, b. p. 112—112·5°/11 mm., D^{23} 0·926, which is oxidisable by potassium permanganate (compare Wohl, Abstr., 1898, i, 556) into *tartardialdehyde diethylacetal*, a viscous oil, b. p. 157—160°/11 mm. The hydrolysis of this acetal is most satisfactorily accomplished by *N*/10-sulphuric acid in the cold, when a sweet solution of *tartardialdehyde* is obtained; this solution on slow evaporation deposits microscopic needles, which, having a bitter taste and being sparingly soluble in water, probably represent a polymeric form; they re-dissolve slowly in warm water, giving a sweet solution, which from its cryoscopic behaviour contains the substance in a unimolecular condition; this solution on evaporation gives a sweet amorphous residue.

The *diphenylhydrazone* of tartardialdehyde forms yellow crystals, m. p. 197·5° (corr., decomp.); no osazone was obtainable; the *di-semicarbazone* has m. p. 227·5° (corr., decomp.); the dioxime, 153·5° (corr., decomp.).

Oxidation of the tartardialdehyde by bromine water gives mesotartaric acid; for this reason the above ethylenic aldehyde is supposed to be that corresponding with maleic acid. D. F. T.

Dihydroxyacetone as an Intermediate Product of Alcoholic Fermentation. ARTHUR SLATOR (*Ber.*, 1912, **45**, 43—46).—It is sometimes assumed that dihydroxyacetone is an intermediate product of the alcoholic fermentation of dextrose (compare Buchner and Meisenheimer, Abstr., 1910, ii, 737). If this is the case, dihydroxyacetone must be fermented by the yeast at least as quickly as

dextrose. Experiments are quoted to show that during twenty minutes no dihydroxyacetone is fermented, although an equal weight of dextrose is entirely fermented by the same yeast during this time. The conclusion is drawn that dihydroxyacetone is not directly fermented, and that it is therefore not an intermediate product of alcoholic fermentation. E. F. A.

The Physico-chemical Bases of the Seliwanoff Lævulose Reaction. HARRY KOENIGSFELD (*Biochem. Zeitsch.*, 1912, **38**, 310—320).—It is shown that the Seliwanoff reaction for lævulose is also yielded by dextrose when the latter is present in a concentration higher than 2%, and also when the hydrochloric acid exceeds 12—12·5% in strength. As the reaction appears to be due to hydroxymethylfurfuraldehyde formed from the lævulose, and as under certain conditions lævulose can be formed from dextrose, the author draws the conclusion that the latter sugar only gives a positive result in the Seliwanoff reaction when the conditions are such that it can be converted in appreciable quantity into the former sugar. This hypothesis is supported by the investigation of the action of acids and bases on dextrose, which, it is shown, probably changes under certain conditions into fructose. S. B. S.

Chemistry of the Wood Dextrins. C. A. YLLNER (*Zeitsch. angew. Chem.*, 1912, **25**, 103—107).—The dextrins obtained by Hönig and Schubert (Abstr., 1887, 125) are mixtures of homologues, from which the individual substances can be obtained only after repeated precipitation. The reducing power increases with the rotation of the dextrin; 1 gram of a dextrin with the rotation $+25°$ corresponds with approximately 0·1 gram of cuprous oxide, a rotation of $+50°$ corresponding with about 0·2 gram of cuprous oxide.

The velocity and extent of hydrolytic decomposition with acids was determined. T. S. P.

Photolytic Decomposition of Smokeless Powders by Ultraviolet Light. Influence of Stabilisers. Damaged Powders. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, **154**, 201—203. Compare this vol., ii, 210).—Exposure of nitroglycerol to the light from a quartz-mercury lamp results in decomposition with production of the following gases: CO_2 (24 vols.), CO (19·5 vols.), N_2 (39 vols.), N_2O (7 vols.), NO (9 vols.), with a considerable amount of nitrogen peroxide, which, however, is not evolved from the gelatinised material treated with stabilisers. At a distance of 20 mm. from the lamp, powders stabilised with amyl alcohol withstood decomposition better than those containing diphenylamine, whereas at 50 mm. diphenylamine was the more effective stabiliser. Damaged French naval powders showed themselves less resistant to the rays than sound powders of the same composition. W. O. W.

General Method for the Preparation of Aliphatic Amines by Catalytic Reduction of Alkyl Nitrites. GEORGES GAUDION (*Ann. Chim. Phys.*, 1912, [viii], **25**, 125—136).—The author has applied Sabatier and Senderens' method (Abstr., 1905, i, 333) of catalytic

reduction by means of finely divided nickel or copper in presence of hydrogen to a series of alkyl nitrites, and finds that these are reduced, giving the corresponding secondary amine, with small amounts of the primary amine and very small quantities of the tertiary amine. Nickel generally acted at a lower temperature than copper; thus in the case of *iso*amyl nitrite the former gave good results at 220—230°, and the latter at 350°.

Several possible explanations of the reaction are discussed, and it is considered that it is best explained by assuming that the alkyl nitrites are first isomerised into the corresponding nitro-paraffins, which are then reduced in the ordinary way. This explanation is the more probable in view of the fact that the reaction seems to take place in the same way as the catalytic reduction of the nitro-paraffins investigated by Sabatier and Senderens (Abstr., 1902, i, 701). T. A. H.

Ammonium and Sulphonium Perchlorates. Relations between Solubility and Constitution. KARL A. HOFMANN, KURT HÖBOLD, and FRITZ QUOOS (*Annalen*, 1912, **386**, 304—317. Compare Abstr., 1910, i, 818; 1911, i, 608).—Ammonium and sulphinium perchlorates are eminently suitable substances for the study of the relationship between solubility and constitution, because they do not form hydrates, are nearly allied crystallographically, and, whilst not being hydrolysed in aqueous solution, are electrolytically dissociated to the same order of magnitude; several factors, therefore, which might possibly mask the relationship are eliminated from the field. The following perchlorates are described (the numbers in brackets denote the grams of water in the saturated solution at 15° containing one gram-molecule of the salt): $NH_4 \cdot ClO_4$ (635); $NHMe_3 \cdot ClO_4$ (800); $NMe_4 \cdot ClO_4$ (32,640); $NMe_3Et \cdot ClO_4$ (1710); $NMe_3Pr \cdot ClO_4$, doubly refracting, rhombic plates or prisms, m. p. 118° (1310); $NMe_3(C_3H_5) \cdot ClO_4$, thin, rectangular plates, m. p. 90° (100); $ClO_4 \cdot NMe_3 \cdot C_4H_9$, almost rectangular plates, m. p. 186° (5810); $ClO_4 \cdot NMe_3 \cdot C_5H_{11}$, doubly refracting, rhombic plates or prisms (10,300); $NMe_3Ph \cdot ClO_4$, rhombic crystals, m. p. 175° (decomp.) (1315); $CH_2I \cdot NMe_3 \cdot ClO_4$, rhombic or monoclinic plates, m. p. 184° (decomp.) (9535); $ClO_4 \cdot NMe_3 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, thin, doubly refracting, rhombic plates, sinters at 86° (150); $NEt_4 \cdot ClO_4$ (6130); $NMeEt_3 \cdot ClO_4$, rhombic plates (915); $NEt_3Pr \cdot ClO_4$, quadratic prisms, m. p. 275° (3090); $NMe_2Et_2 \cdot ClO_4$ (150); $C_2H_4(NH_3 \cdot ClO_4)_2$, rhombic plates (200); $C_2H_4(NMe_3 \cdot ClO_4)_2$, stout, rhombic plates (28,700); $C_3H_6(NMe_3 \cdot ClO_4)_2$, doubly refracting leaflets (23,500); $SMe_3 \cdot ClO_4$, stout, rhombic prisms or elongated plates, m. p. above 267° (1280); $SMe_2Et \cdot ClO_4$, elongated, rhombic plates (840); $SMe_2Pr \cdot ClO_4$ (1700); $ClO_4 \cdot SMe_2 \cdot C_4H_9$ (1650); $C_2H_4(SMe_2 \cdot ClO_4)_2$, rhombic prisms, m. p. 250° (2360);

$$ClO_4 \cdot SMe_2 \cdot CH{:}CH_2,$$

elongated plates (1368); $C_3H_6(SMe_2 \cdot ClO_4)_2$ (2480).

The most striking result is the sparing solubility of the quaternary ammonium perchlorates in comparison with the great solubility of methylammonium perchlorate (120), dimethylammonium perchlorate (70), diethylammonium perchlorate (115), and ethylammonium perchlorate (70). Another striking fact is the enormous difference in the

solubilities of quaternary ammonium perchlorates containing like alkyl groups from those containing unlike alkyl groups; for example, $NMe_4 \cdot ClO_4$ (32,640), $NMe_3Et \cdot ClO_4$ (1710). These two groups of perchlorates also differ in their stability towards alkaline potassium permanganate, those of the type $NR_4 \cdot ClO_4$ being stable, whilst members of the other group are rapidly oxidised, at the ordinary temperature.

The molecular dilutions of glyceryltrimethylammonium perchlorate (150) and of choline perchlorate (70) show how enormously the solubility is increased by the introduction of hydroxyl groups; when the hydroxyl groups are esterified, however, the solubility is very largely diminished, as shown in the case of nitratocholine perchlorate (40,000). Deductions similar to the preceding can be drawn in the case of the sulphinium perchlorates. C. S.

Decomposition of Quaternary Ammonium Hydroxides. II. JULIUS VON BRAUN (*Annalen*, 1912, **386**, 273—303. Compare Abstr., 1911, i, 610).—The decomposition by heat of diammonium hydroxides of the type $OH \cdot NMe_3 \cdot [CH_2]_x \cdot NMe_3 \cdot OH$ may result in the formation of di-olefines, unsaturated tertiary amines, or ditertiary diamines. Substances in which x is 3, 5, 7 and 10, have been examined. All four yield by decomposition unsaturated tertiary amines, $CH_2{:}CH \cdot [CH_2]_{x-2} \cdot NMe_2$, the amount of which increases as x increases; thus *hexamethyldecylenediammonium iodide*,

$$I \cdot NMe_3 \cdot [CH_2]_{10} \cdot NMe_3I,$$

white leaflets, m. p. 231°, obtained from $\alpha\kappa$-di-iododecane (Abstr., 1910, i, 25) and alcoholic trimethylamine at 100°, is converted by the usual treatment into a syrupy mass of *hexamethyldecylenediammonium hydroxide*, by the distillation of which very little di-olefine (unexamined) is formed, the chief product being a mixture of 30% of *dimethyldecenylamine*, $CH_2{:}CH \cdot [CH_2]_8 \cdot NMe_2$, b. p. 118—120°/17 mm. (*platinichloride*; *picrate*, m. p. 137°; *methiodide*, m. p. 137—140°), and 50% of *ακ-tetramethyldiaminodecane*, $C_{14}H_{32}N_2$, b. p. 157—158°/17 mm., (*platinichloride*, m. p. 189° [decomp.]; *picrate*, m. p. 139—140°). The distillation of trimethyldecenylammonium hydroxide gives a 75% yield of dimethyldecenylamine; hence the latter can be obtained from hexamethyldecylenediammonium hydroxide with comparative ease and in good yield.

Hexamethylheptylenediammonium bromide,

$$Br \cdot NMe_3 \cdot [CH_2]_7 \cdot NMe_3 \cdot Br,$$

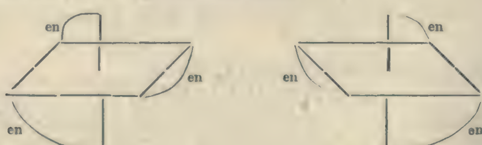
m. p. 245°, prepared from $\alpha\eta$-dibromoheptane and alcoholic trimethylamine at 100°, forms a diammonium hydroxide, the distillation of which yields about 15% of a heptadiene, 28—29% of *dimethylheptenylamine*, $CH_2{:}CH \cdot [CH_2]_5 \cdot NMe_2$, b. p. 166—169° or 60—65°/10 mm. (*picrate*, m. p. 88°; *methiodide*, m. p. 120°), and 51% of *αη-tetramethyldiaminoheptane*, $NMe_2 \cdot [CH_2]_7 \cdot NMe_2$, b. p. 225—230° (decomp.) or 101—102°/10 mm. (*picrate*, m. p. 136°; *dimethiodide*, m. p. 242°). Unlike the two preceding diammonium hydroxides, hexamethylamylenediammonium hydroxide, prepared from the iodide (*loc. cit.*), begins to decompose during the evaporation of its aqueous solution. Its complete decomposition yields mainly trimethylamine, water, and piperylene, very little *tetramethyldiaminopentane*, b. p. 193—194°

(*platinichloride*, m. p. 218° [decomp.]; *picrate*, m. p. 149°), and *dimethylpentenylamine* (isolated as the *methiodide*, m. p. 200°) being produced. Similar results are obtained by the decomposition of hexamethylbutylenediammonium hydroxide and hexamethylpropylenediammonium hydroxide; in the latter case, the non-nitrogenous product is not allene, but a mixture of viscous oxidation products, from which an unsaturated substance, $C_6H_{10}O$ (*semicarbazone*, m. p. 192°), probably an isomeride, $CH_3\cdot CO\cdot CH_2\cdot CMe{:}CH_2$, of mesityl oxide, has been isolated.

The experiments indicate that in the decomposition of diammonium hydroxides, whilst the lower members of the series decompose simultaneously at both ends of the chain, the higher members experience changes first at one end of the chain only. For example: $OH\cdot NMe_3\cdot[CH_2]_{10}\cdot NMe_3\cdot OH \longrightarrow Me\cdot OH + OH\cdot NMe_3\cdot[CH_2]_{10}\cdot NMe_2$ and $H_2O + NMe_3 + OH\cdot NMe_3\cdot[CH_2]_8\cdot CH{:}CH_2$; then $OH\cdot NMe_3\cdot[CH_2]_{10}\cdot NMe_2 \longrightarrow MeOH + NMe_2\cdot[CH_2]_{10}\cdot NMe_2$ and $H_2O + NMe_3 + CH_2{:}CH\cdot[CH_2]_8\cdot NMe_2$, whilst $OH\cdot NMe_3\cdot[CH_2]_8\cdot CH{:}CH_2 \longrightarrow MeOH + NMe_2\cdot[CH_2]_8\cdot CH{:}CH_2$ and $H_2O + NMe_3 + C_{10}H_{18}$.

It has been shown (*loc. cit.*) that the presence of an ethylenic linking in an aliphatic group in a quaternary ammonium hydroxide facilitates the elimination of the group when the point of unsaturation is adjacent to the nitrogen atom. The decomposition of the hydroxides $OH\cdot NMe_3\cdot[CH_2]_x\cdot CH{:}CH_2$ shows that the loosening influence of the ethylenic linking weakens as its distance from the nitrogen atom increases; trimethyldecenylammonium hydroxide yields not more hydrocarbon than does the corresponding saturated quaternary ammonium hydroxide. C. S.

The Asymmetric Cobalt Atom. V. ALFRED WERNER (*Ber.*, 1912, 45, 121—130).—According to the author's theory, there are two possible salts of triethylenediaminecobalt which stand to each other in the relation of object and mirror-image, and are not superposable. These may be represented thus:



Such compounds form the simplest possible case of molecular asymmetry, being specially characterised by having all the co-ordination positions of the central atom occupied by structurally identical groups, the asymmetry being caused by the special spatial arrangement of these groups. Such asymmetry the author denotes as *molecular asymmetry II* (compare Abstr., 1911, i, 838), and he has been successful in resolving some of the salts into the optically active isomerides. Resolution by means of the camphorsulphonates, α-bromocamphorsulphonates, etc., was unsuccessful, since the salts would not crystallise. Triethylenediaminecobaltic tartrate was obtained in the

crystalline condition, however, and proved to be a partial racemate, which underwent slight resolution on fractional crystallisation, the extent of the resolution being ascertained by taking advantage of the very strong rotation dispersion of these compounds. The lesser soluble crystals contained an excess of the lævo-isomeride, the final mother liquors containing the excess of the dextro-isomeride; the pure isomerides could then be isolated by making use of the fact that their bromides were readily soluble in concentrated hydrobromic acid, the racemic bromide being almost insoluble. The yields of the active components were very poor by this method, which was then replaced by the following: The chloride tartrate, $\left[\text{Co en}_3\right]^{\text{Cl}}_{C_4H_4O_6}$, does not form a partial racemate, and by one recrystallisation can be separated into the sparingly soluble *d*-triethylenediaminecobaltic chloride-*d*-tartrate and the readily soluble *l*-triethylenediaminecobaltic chloride-*d*-tartrate, from which other salts can be obtained without difficulty. The bromide tartrates behave similarly to the chloride tartrates.

The specific rotations of the various salts are very large, and the rotation dispersion is very marked, as shown by the following table:

	$[\alpha]_D$.	$[\alpha]_C$.	$[M]_D$.	$[M]_C$.
Chloride	+152° −154	±45°	+552·5° −560	±153·6°
Bromide	+117 −115	±32	+602·5 −592	±165
Nitrate	+132 −130	+46 −44	+561 −552	+195·5 −187

The active salts are very stable; their solutions can be evaporated down with concentrated hydrochloric or hydrobromic acid without suffering any loss of activity. The active isomerides are much more readily soluble than the racemates.

The triethylenediaminecobaltic salts, $(\text{Co en}_3)X_3$, are best prepared as follows: 10 grams of cobalt chloride are dissolved in 150 grams of 10% ethylenediamine and oxidised by leading air through the solution. The brown solution so obtained is acidified with hydrochloric acid, evaporated to crystallisation, the crystals dissolved in water, and ammonium nitrate added to the solution, whereby 1:6-dichlorodiethylenediaminecobaltic nitrate is precipitated. After collecting this salt the filtrate is precipitated with sodium bromide, giving pure triethylenediaminecobaltic bromide.

Triethylenediaminecobaltic tartrate, $(\text{Co en}_3)_2(C_4H_4O_6)_3$, is obtained from the bromide by double decomposition with silver tartrate; it crystallises in spherical aggregates of light yellow needles. *Triethylenediaminecobaltic chloride-tartrate*, $\left[\text{Co en}_3\right]^{\text{Cl}}_{C_4H_4O_6}$, is prepared by interaction of 1 molecule of the chloride with 1 molecule of silver tartrate, the precipitate of silver chloride being extracted with boiling water until pure white in colour. The solutions thus obtained are concentrated and allowed to crystallise, columnar and tabular crystals separating; these are collected and the filtrate further concentrated.

A second crop of crystals often separates, and then the concentrated solution sets to a jelly-like mass. The crystals consist of d-*triethylenediaminecobaltic chloride-tartrate*, $\left[\mathrm{Co\ en_3}\right]^{\mathrm{Cl}}_{\mathrm{C_4H_4O_6}},5H_2O$, and are purified by one recrystallisation from water; they have $[\alpha]_D +101°$, $[M]_D +517·6°$, $[\alpha]_C +35°$, $[M]_C +179·4°$. The gel consists of the corresponding *laevo*-salt, mixed with small quantities of the *d*-isomeride.

d-*Triethylenediaminecobaltic bromide-tartrate*, $\left[\mathrm{Co\ en_3}\right]^{\mathrm{Br}}_{\mathrm{C_4H_4O_6}},5H_2O$, is obtained similarly, and forms a felted mass of light yellow, silky needles, which, in contact with the solution, slowly change to much darker, stout, plate-shaped crystals; they have $[\alpha]_D + 98°$, $[M]_D + 555°$, $[\alpha]_C + 38°$, $[M]_C + 211·7°$. The corresponding *laevo*-isomeride forms a gel.

d-*Triethylenediaminecobaltic bromide*, $[\mathrm{Co\ en_3}]Br_3,2H_2O$, is prepared from either the bromide-tartrate or the chloride-tartrate by trituration with warm concentrated hydrobromic acid. The solution, after filtering, deposits large, hexagonal plates, which are probably an acid bromide; on recrystallisation from water, large, columnar crystals of the bromide are obtained. The l-*bromide*, $[\mathrm{Co\ en_3}]Br_3,2H_2O$, is similarly prepared from the gel of *l*-bromide-tartrate or *l*-chloride-tartrate, the sparingly soluble racemic bromide remaining undissolved. The d- and l-*chlorides*, $[\mathrm{Co\ en_3}]Cl_3,H_2O$, are obtained from the bromides by reaction with silver chloride; they crystallise in small, golden-yellow, needle-shaped crystals. The d- and l-*nitrates*, $[\mathrm{Co\ en_3}](NO_3)_3$, are prepared from the bromide by treatment with the theoretical quantity of silver nitrate; they form pyramidal crystals, which are readily soluble in water. T. S. P.

Preparation of Hexamethylenetetramine Borocitrates. ATHENSTAEDT and REDEKER (D.R.-P. 238962).—Alkali and magnesium borocitrates have been previously described. The hexamethylenetetramine derivatives have now been obtained by thoroughly mixing the required proportions of the ingredients in either concentrated aqueous or alcoholic solution. They form colourless, crystalline powders, and are readily soluble in water or alcohol.

Hexamethylenetetramine borocitrates having the following composition are mentioned:

$C_6H_8O_7,3HBO_2,2C_6H_{12}N_4$, decomp. 182°;
$C_6H_8O_7,3HBO_2,3C_6H_{12}N_4$ „ 192°;
$2C_6H_8O_7,2HBO_2,3C_6H_{12}N_4$ „ 185°;
$2C_6H_8O_7,4HBO_2,3C_6H_{12}N_4$ „ 180°;
$2C_6H_8O_7,6HBO_2,3C_6H_{12}N_4$ „ 178°.

F. M. G. M.

Compounds of Chromic Hydroxide with Amino-acids Derived from Proteins. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1912, **154**, 119—120).—Chromic hydroxide (1 mol.) dissolved in a boiling aqueous solution of glycine (6 mols.) gives a purple-red solution which deposits red crystals containing four molecules of the amino-acid and two hydroxyl groups to two atoms

of chromium. The excess of chromic hydroxide is removed by lixiviation or treatment with acid. The filtrate from the red crystals on slow evaporation deposits brilliant, vermilion, acicular prisms of a compound containing six molecules of the amino-acid to two atoms of chromium. Both compounds are soluble in acids, and are slowly decomposed by alkalis. They do not show the ordinary reactions of chromium salts, but resemble more closely the chromoxalates.

W. O. W.

Action of Amino-acids on Sugars; Formation of Substances Resembling Melanins. LOUIS C. MAILLARD (*Compt. rend.*, 1912, 154, 66—68. Compare this vol., i, 13).—Continuing his experiments on the action of natural polyhydric alcohols on amino-acids, the author finds that when glycine is heated on the water-bath with four times its weight of dextrose and the same amount of water, it rapidly loses carbon dioxide and forms dark brown, cyclic; condensation products, the molecules of which contain at least two dextrose residues to one nitrogen atom. They are said to be identical with the melanin pigments obtained in the hydrolysis of proteins. If this is so, the comparatively low yield of amino-acids in such hydrolyses receives an explanation. The reaction is instantaneous between glycine and xylose or arabinose, rapid in the case of galactose and mannose, slow with lactose and maltose, whilst several hours elapse before it occurs in the case of sucrose. Of the common amino-acids, alanine is the most active.

W. O. W.

The Action of Moist Sulphur on Cholic Acid and Taurine. J. A. A. AUZIES (*Rev. gen. chim. pure appl.*, 1911, 14, 278—280).—A study of the composition of the gall and bile of cattle and pigs, from which the author corroborates the results of Langheld (Abstr., 1908, ii, 211).

Cholic acid, $OH\cdot NMe_3\cdot CH_2\cdot CO_2H$, is prepared by mixing calcium chloroacetate (1·92 parts) with trimethylamine (1·18 parts) and heating the *chloride* of *calcium trimethylammoniumacetate* so obtained with milk of lime at 120—150°.

Taurine is prepared on an industrial scale as follows: Acetaldehyde is heated at 140° with chlorosulphonic acid,

$$CH_3\cdot CHO + SO_3HCl = HCl + SO_3H\cdot CH_2\cdot CHO,$$

the product converted into its calcium salt, $(CHO\cdot CH_2\cdot SO_3)_2Ca$, which by treatment with ammonium hydroxide yields the aldehyde ammonia, $[NH_2\cdot CH(OH)\cdot CH_2\cdot SO_3]_2Ca$, this loses water (2 mols.) on heating, and is converted into the imine, $(NH\colon CH\cdot CH_2\cdot SO_3)_2Ca$, which after reduction to the corresponding amine and elimination of calcium with sulphuric acid furnishes the required taurine.

F. M. G. M.

Preparation of Bromoacyl*iso*carbamide Ethers. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 240353).—When *iso*carbamide ethers of the general formula $NH_2\cdot C(OR)\colon NH$ (R = alkyl or alkylaryl) are treated with bromodiethylacetyl halides, they yield bromo-α-ethylbutyryl*iso*carbamide ethers, which are of therapeutic value.

*Bromo-α-ethylbutyryl*iso*carbamide methyl ether*, colourless crystals, m. p. 72°, was obtained by boiling bromo-α-ethylbutyryl bromide with

methyl *iso*carbamide hydrochloride (Abstr., 1900, i, 340) in aqueous solution, cooling, and rendering alkaline when the product separated.

F. M. G. M.

Specific Rotatory Power of Glutamine. Ammonium Glutamate. Ernst Schulze and Georg Trier (*Ber.*, 1912, **45**, 257—262).—Supposed pure preparations of glutamine obtained from different plant preparations by precipitation with mercuric nitrate and continued crystallisation show $[\alpha]_D$ varying from $+5{\cdot}4°$ to $8{\cdot}9°$. By purification of the copper salt, these preparations all yield glutamine of constant rotatory power, $[\alpha]_D$ $+6°$ to $7°$. The higher values are due to the presence of traces of glutamic acid, which, acting as an acid, increases the rotatory power of glutamine.

Glutamic acid forms a monobasic *ammonium* salt, $[\alpha]_D$ $-3{\cdot}6°$, which begins to lose ammonia when kept over concentrated sulphuric acid, and readily loses ammonia when evaporated in aqueous solution. Since glutamine when boiled in aqueous solution is to some extent hydrolysed to the ammonium salt, the presence of glutamic acid is explained.

E. F. A.

Action of Ammonia on Ammonium Thiocyanate. Walter P. Bradley and W. B. Alexander (*J. Amer. Chem. Soc.*, 1912, **34**, 15—24).—Comparatively few substances become deliquescent on exposure to dry ammonia, and of these ammonium thiocyanate appears to possess the property in the highest degree, the deliquescence continuing up to a temperature of 88°. The absorptive power of the salt was determined at various temperatures between 0° and 100°. At 0°, the product contained 43·10% of ammonia; at 25°, 31·16%; at 50°, 19·40%; at 75°, 6·17%, whilst at 100° none was absorbed. F.-p. determinations were made of solutions of ammonium thiocyanate in ammonia, the concentrations ranging from 0% to 100% of the latter. On plotting the results, it is shown that there are certainly three, and probably five, compounds formed. The former are: NH_4CNS,NH_3, m. p. $-16°$ (metastable); $NH_4CNS,3NH_3$, m. p. $-38°$; and

$$NH_4CNS,8NH_3,$$

m. p. about $-87°$. The other two compounds are $NH_4CNS,6NH_3$, m. p. $-76°$, and $NH_4CNS,7NH_3$, m. p. $-84°$. Indications were also obtained of the possible existence of the compound

$$2NH_4CNS,13NH_3,$$

m. p. about $-80°$. The lowest eutectic point was in the vicinity of $-96°$.

E. G.

The Composition of Prussian Blue. P. Woringer (*Chem. Zeit.*, 1912, **36**, 78).—Evidence for regarding Prussian blue as a ferrocyanide has been given by Hofmann, Heine, and Höchtlen (Abstr., 1905, i, 38). On the other hand, when a ferric salt is precipitated with an excess of potassium ferrocyanide, the filtrate contains considerable quantities of potassium ferricyanide, formed by the reactions: $FeCl_3 + K_4Fe(CN)_6 = FeCl_2 + K_3Fe(CN)_6 + KCl = KFeFe(CN)_6 + 3KCl$, and in the filtrate, $3KFeFe(CN)_6 = Fe_3[Fe(CN)_6]_2 + K_3Fe(CN)_6$.

If ammonium carbonate solution is added to a boiling suspension of

Prussian blue, ammonium ferricyanide as well as ferrocyanide is found in the filtrate, and the iron remains as Fe_3O_4. This is considered to prove that Prussian blue is a ferricyanide. C. H. D.

Organic Boro-Nitrogen Compounds. ARDEN RICHARD JOHNSON (*J. Physical Chem.*, 1912, 16, 1—28).—A series of compounds of boron tribromide with amines and nitriles was prepared in which boron as well as nitrogen is supposed to function as quinquevalent. Various additive compounds of boron trichloride, tribromide, and tri-iodide with ammonia are known, in which the proportion of ammonia varies from 1·5 to 15 molecules per molecule of boron compound.

Boron tribromide reacts with amines and nitriles with liberation of heat, and additive compounds of the type $(X)N\vdots BBr_3$ are apparently formed in most cases. The nitriles and tertiary amines, except trimethylamine, give fairly stable crystalline products. Compounds of this type were also isolated from the primary *iso*amylamine and aniline. The compounds of the aliphatic secondary amines immediately lose hydrogen bromide, amorphous products of the type $R_2N\cdot BBr_2$ resulting. Similarly, the product from ethylamine has the constitution $NHEt\cdot BBr_2$ With methylamine, the reaction apparently goes a stage further, and the product isolated has the formula $B(NHMe)_2Br$. Piperidine and diphenylamine give compounds of the type $(YNH)_3,BBr_3$.

The compounds were prepared by passing the dry gaseous amines into a carbon tetrachloride solution of boron tribromide or by adding the bromide solution from a burette to the anhydrous amine or nitrile dissolved in carbon tetrachloride. In some cases an oily insoluble product containing excess of amine was first formed, and afterwards converted into a solid product by further addition of bromide.

The *substances*, $(NHMe)_2\vdots BBr$, $NHEt\cdot BBr_2$, $NH_2(C_5H_{11})\vdots BBr_3$, $NH_2Ph\vdots BBr_3$, $NMe_2\cdot BBr_2$, and $NPr_2\cdot BBr_2$, are white, amorphous solids sparingly soluble in carbon tetrachloride. The mono*iso*amylamine compound, which may be handled in the air, turns yellow in sunlight, but does not dissociate very rapidly below 40°. When heated up quickly, it appears to melt and decompose simultaneously. It burns furiously, colouring the flame intensely green.

The iso*amyl* compound, $N(C_5H_{11})_2\vdots BBr_2$, may be crystallised from carbon tetrachloride. It dissolves in water, giving di*iso*amylamine hydrobromide and boric acid. The *substance*, $3C_5H_{11}N,BBr_3$, is formed from piperidine in a violent reaction, which must be moderated by careful cooling. It has been obtained as a pale yellow precipitate, which readily loses hydrogen bromide when exposed over sodium hydroxide in a desiccator, being converted into the *substance*,

$$C_5H_{10}N\cdot BBr_2(C_5H_{11}N)_2.$$

The latter is a stable solid giving greenish-yellow, fluorescing solutions in organic solvents. The *substance*, $3NHPh_2,BBr_3$, is a white precipitate comparatively stable in air.

Trimethylamine reacts with boron tribromide with development of heat. White fumes were given off, and no solid compound could be

isolated. The *substance*, $NEt_3\colon BBr_3$, crystallises from carbon tetrachloride in long, slender prisms. The *substance*, $NMe_2Ph\colon BBr_3$, forms a camphor-like, crystalline, hygroscopic mass. When exposed in a desiccator over sodium hydroxide, the elements of methyl bromide are removed, and the *substance*, $NMePh\cdot BBr_2$, remains. The latter is very rapidly decomposed by hot alkali with precipitation of boron nitride, BN. The *pyridine* compound, $C_5H_5N\colon BBr_3$, is a snow-white, amorphous mass, fairly stable in the air, but tending to dissociate with rising temperature; at 120° it turns brown and sinters. When placed in a desiccator over sodium hydroxide, the elements of hydrogen bromide are removed, and the *substance*, $C_5H_4N\cdot BBr_2$, remains as a stable powder. It is suggested that boron is probably combined with the carbon as well as the nitrogen of the pyridine nucleus in this compound. The white *substance*, $C_9H_7N\colon BBr_3$, formed from quinoline is more stable than the pyridine compound, and scarcely fumes in the air.

The *substances*, $CNMe\colon BBr_3$, $CNEt\colon BBr_3$, and $CNPh\colon BBr_3$, are obtained from their carbon tetrachloride solutions as white crystals. The methyl compound dissociates very rapidly at 30°, and the ethyl compound is slightly more stable. The *substance*, $CH_2Ph\cdot CN\colon BBr_3$, which is difficult to purify by crystallisation, was obtained as a slightly yellow, crystalline mass. It melts with some decomposition.

Most of the above boron tribromide compounds decompose or sublime without melting. Some of the nitrile compounds may be heated to nearly 200° before decomposing. Of the amine products those of pyridine and quinoline are the most stable. The products of decomposition by heat probably contain boron nitride in most cases. The substances described are violently decomposed by water, absolute alcohol, acetaldehyde, and acetic acid, the products containing boric acid accompanied by hydrogen bromide, ethyl bromide, bromoacetaldehyde, and acetyl bromide respectively. Acetone, the esters, and ether have a less violent action, and crystalline products containing boron and carbon have been obtained. Hydrocarbons usually exert no solvent action on boron bromide compounds, but with prolonged contact in sunlight the hydrocarbon assumes a red to brown tint. A slow decomposition also occurs in contact with chloroform and bromoform. Carbon tetrachloride and tetrabromide, in which the substances are but slightly soluble, have no chemical action on them. R. J. C.

Preparation of Methyl*cyclo*pentane. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1611—1613).—The preparation of methyl*cyclo*pentane by the action of fuming hydriodic acid at 100—105° on *cyclo*pentanylcarbinol (compare Zelinsky, Abstr., 1908, i, 727) and reduction of the iodide thus obtained by means of zinc dust in aqueous alcoholic solution gives a product containing *cyclo*hexane. Hence, when heated with hydriodic acid, the *cyclo*pentanylcarbinol undergoes partial isomerisation into a six-carbon atom ring compound. Similar cases of the ready isomerisation of substituted cyclic carbinols have been observed by Demjanoff (Abstr., 1910, i, 838) and by Kijner (Abstr., 1905, i, 772; 1908, i, 530, 864; 1911, i, 42). T. H. P.

Polymerisation of Diethylene Hydrocarbons. Polymerisation of *as*-Dimethylallene. IV. SERGIUS V. LEBEDEFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1735—1739).—For an unsymmetrical disubstituted allene, six dimerides are possible, three of each of the types: $\begin{array}{l}C{-}C{:}C\\ \mid\quad\mid\\ C{-}C{:}C\end{array}$ and $\begin{array}{l}\quad C{-}C{=}C\\ \quad\ \mid\quad\mid\\ C{=}C{-}C\end{array}$. Two of the compounds of the former of these types have been obtained (Abstr., 1911, i, 774), failure to isolate the third being due probably to its high velocity of polymerisation. The author's results indicate that the velocity of polymerisation of hydrocarbons with conjugated systems of double linkings, $:C{:}\underset{\bullet}{C}\cdot\underset{\bullet}{C}{:}C:$, increases with diminution of the loading of the extreme carbon atoms and with increase of that of the intermediate ones. Hence, of the three dimerides of *as*-dimethylallene of the first type, 1 : 2-di*iso*propenyl*cyclo*butane should be the most stable, 1 : 1 : 2 : 2-tetramethyl-3 : 4-dimethylene*cyclo*butane should occupy an intermediate position in this respect (*loc. cit.*), and the third, 3 : 3-dimethyl-2-methylene-1-*iso*propenyl*cyclo*butane, should readily polymerise. By the choice of suitable conditions, the remaining dimeride (the second) has now been obtained.

1 : 1 : 2 : 2-*Tetramethyl*-3 : 4-*dimethylene*cyclo*butane*,

$$CH_2{:}C\Big\langle\begin{matrix}C({:}CH_2)\\ CMe_2\end{matrix}\Big\rangle CMe_2,$$

has b. p. 140—141°/760 mm., 66—67°/55 mm., D_4^{20} 0·7927, n_D^{20} 1·46063, n_C^{20} 1·45701, n_F^{20} 1·46988, n_G^{20} 1·47807, and yields tetramethylsuccinic acid when treated with ozone.

The physical properties of these three dimerides, some of which were given wrongly in the previous paper, are as follows:

	B. p.	D_4^{20}.	Optical exaltation.
1 : 2-D*iso*propenyl*cyclo*butane	179—181°	0·8422	2·34
1 : 1-Dimethyl-2-methylene-3-*iso*propenyl*cyclo*butane	149—150	0·7982	2·09
1 : 1 : 2 : 2-Tetramethyl-3 : 4-dimethylene*cyclo*butane	140—141	0 7927	1·81

As regards the non-formation of dimerides of the second of the two types given above, it is pointed out that the relations of unsaturated compounds to reactions of combination indicate clearly that the tensions of the affinities in the molecule are distributed unequally. For the complex $:C{:}C{:}C:$ they are directed the most strongly towards the middle carbon atom, so that combination of the two molecules takes place first at this place, there being possible the two annexed arrangements.

$$\begin{array}{ccc} CH_2{:}\overset{2}{C}{:}\overset{3}{C}Me_2 & & \overset{1}{CH_2}{=}\overset{2}{C}{:}\overset{3}{C}Me_2 \\ \vdots & \text{and} & \vdots \\ \underset{1}{CH_2}{:}\underset{2}{C}{:}\underset{3}{C}Me_2 & & \underset{3}{CMe_2}{:}\underset{2}{C}{:}\underset{1}{CH_2}\end{array}$$

With the former of these arrangements, further saturation of the free affinities gives the two dimerides, 1 : 2-di*iso*propenyl*cyclo*butane and 1 : 1 : 2 : 2-tetramethyl-3 : 4-dimethylene*cyclo*butane, whilst with the latter, owing to its symmetrical character, only one dimeride, namely, 1 : 1-dimethyl-2-methylene-3-*iso*propenyl*cyclo*butane, is obtained. This scheme hence excludes the possibility of formation of dimerides of the second type.

T. H. P.

Chemical Action of Light. XXII. Autoxidations. I. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1912, **45**, 38—43; *Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 673—677).—Aromatic hydrocarbons on prolonged exposure to the action of light in presence of water in an atmosphere of oxygen in sealed vessels are partly oxidised to the corresponding carboxylic acids; small quantities of the corresponding aldehydes and of formic acid are also formed.

Thus toluene yields benzoic acid and benzaldehyde; *p*-xylene gives *p*-toluic acid, m. p. 181°, and a little terephthalic acid, as well as traces of the aldehyde; *m*-xylene forms *m*-toluic acid, m. p. 111°, and *iso*phthalic acid; *o*-xylene forms *o*-toluic acid, m. p. 107—108°. *p*-Cymene yields some aldehyde, *p*-cuminic acid, m. p. 119°, *p*-propenylbenzoic acid, m. p. 165°, and α-hydroxy-*p*-cuminic acid, m. p. 156°.

In the dark the hydrocarbons are unchanged. *p*- and *o*- Nitrotoluene, also phenanthrene, are practically unaltered after prolonged exposure to light. E. F. A.

[Orientation in the Benzene Nucleus.] JULIUS OBERMILLER (*Ber.*, 1912, **45**, 165—167. Compare Abstr., 1911, i, 960).—The author upholds his claim of priority over Holleman (this vol., i, 20), and maintains that there is no essential difference between their views concerning substitution in the benzene nucleus. F. B.

Benzene Hexachlorides and their Decomposition into Trichlorobenzenes. T. VAN DER LINDEN (*Ber.*, 1912, **45**, 231—247). —α- and β-Benzene hexachlorides, prepared by the action of chlorine on benzene in sunlight, form a eutectic solidifying at 155·5°. This point was mistaken for the melting point by Matthews (Trans., 1891, **59**, 166). In addition to the α- and β-isomerides, two new benzene hexachlorides are formed in the reaction: all four compounds are stereoisomerides. The γ-*isomeride* crystallises in needles and lozenge-shaped forms, m. p. 112—113°; the δ-*isomeride* forms slender, lustrous, twin platelets, m. p. 129—132°.

On decomposition of α-benzene hexachloride with alkali, a mixture of 1 : 2 : 4-, 1 : 2 : 3-, and 1 : 3 : 5-trichlorobenzenes is obtained. The temperature at which decomposition is effected has no influence on the relative proportions of these, or is this proportion altered on replacing potassium hydroxide by sodium hydroxide or substituting methyl alcohol for ethyl alcohol. The proportion is, however, altered by the use of pyridine or quinoline, more of the 1 : 2 : 4- and less of the 1 : 2 : 3-isomeride being obtained, the amount of the 1 : 3 : 5-trichlorobenzene remaining constant.

β-Benzene hexachloride, when decomposed by potassium hydroxide in ethyl alcohol, yields the same three trichlorobenzenes as the α-isomeride, but in different proportions, which are very similar to those obtained on decomposing the α-isomeride with pyridine. Pyridine, however, has hardly any action on the β-compound.

γ-Benzene hexachloride yields the three trichlorobenzenes in slightly different proportions than either of the α- or β-isomerides.

It was not found possible to eliminate the chlorine in stages, neither

could hydrogen chloride be split off by means of aluminium or ferric chlorides.

The fact that a considerable proportion of 1 : 2 : 3-trichlorobenzene is formed indicates that the elimination of hydrogen chloride is not entirely between two neighbouring carbon atoms. E. F. A.

Preparation of γ-Chloropropylbenzene and its Homologues. EMANUEL MERCK (D.R.-P. 239076).—*γ-Chloropropylbenzene*,

$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2Cl$,

a colourless oil with penetrating odour, b. p. 219—220° or 110°/21 mm., is obtained in 78% yield from γ-chloropropylaniline by diazotisation and subsequent reduction with stannous chloride in alkaline solution. F. M. G. M.

2-Chloro-3 : 5-dinitrotoluene. WALTHER BORSCHE and ANNA FIEDLER (*Ber.*, 1911, **45**, 270—273).—2-Chloro-3 : 5-dinitrotoluene is formed in only small quantity by nitrating *o*-chlorotoluene, and does not constitute the main product of the reaction as stated by Nietzki and Rehe (Abstr., 1893, i, 15). It crystallises from alcohol in stout, yellow rhombs, m. p. 63—64°; Nietzki and Rehe give 45°. It is best prepared by heating 2-chloro-3-nitrotoluene or 2-chloro-5-nitrotoluene with a mixture of equal parts of sulphuric and fuming nitric acids for two hours on the water-bath.

The above-mentioned mononitro-compounds are conveniently prepared by nitrating aceto-*o*-toluidide and hydrolysing the product with hydrochloric acid; the resulting mixture of 3-nitro- and 5-nitro-*o*-toluidine is separated by steam distillation, and the amino-group replaced by chlorine according to Ullmann's method.

4-Chloro-3 : 5-dinitrotoluene has m. p. 116—117°, and not 48° as given by Hönig (Abstr., 1887, 1034). F. B.

Conversion of the Bromonitrobenzenes into the Corresponding Dichlorobenzenes by Phosphorus Pentachloride. JULIUS SCHMIDT and HANS WAGNER (*Annalen*, 1912, **387**, 164—165).—When heated with phosphorus pentachloride in a sealed tube at 180° for six hours, *o*-, *m*-, and *p*-bromonitrobenzenes are converted more or less smoothly into *o*-, *m*-, and *p*-dichlorobenzenes. C. S.

Action of Nitric Acid on *cyclo*Pentane and Methyl*cyclo*pentane. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1603—1611. Compare Abstr., 1910, i, 830).—*Nitro*cyclo*pentane*, $C_5H_9 \cdot NO_2$, obtained by the interaction of aluminium nitrate and *cyclo*pentane in a sealed tube, is a colourless liquid, b. p. 90—91°/40 mm., D_4^{23} 1·0776, n_D^{23} 1·4518, with the characteristic odour of secondary nitro-compounds. On oxidation with nitric acid, it yields glutaric acid, which is also formed when *cyclo*pentane itself is oxidised.

Nitration of methyl*cyclo*pentane by means of nitric acid yields 1-nitro-1-methyl*cyclo*pentane and 2-nitro-1-methyl*cyclo*pentane, b. p. 98—99°/40 mm., D_4^{22} 1·0381, n_D^{22} 1·4488 (compare Markownikoff, Abstr., 1899, i, 799).

Thus, in the secondary nitro-product of methyl*cyclo*pentane the

nitro-group occupies the α-position, whilst in that of methyl*cyclo*hexane it occupies the β-position.

The above two nitro-compounds formed by the nitration of methyl*cyclo*pentane are accompanied by succinic and α-methylglutaric acids; probable schemes are given for the formation of these two acids.
T. H. P.

The Preparation of ω-2-Dinitrotoluene, its Homologues and Derivatives. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 239953).—ω-2-*Dinitrotoluene*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NO_2$ or

$$NO_2\cdot C_6H_4\cdot CH\vdots NO(OH),$$

m. p. 67°, is readily prepared in 70% yield by heating *o*-nitrotoluene (2 parts) at 110—120° during eight hours with the gradual addition of 70% nitric acid (1 part), *o*-nitrobenzaldehyde and *o*-nitrobenzoic acid being simultaneously produced as by-products. The following compounds are described: ω-4-*dinitrotoluene*, m. p. 91°; 4-*chloro*-ω-2-*dinitrotoluene*, m. p. 112°; 4-*bromo*-ω-2-*dinitrotoluene*, m. p. 113·5°; 6-*chloro*-ω-2-*dinitrotoluene*, m. p. 82°; whilst *o*-nitro-*m*-xylene yields a mixture of ω-6-*dinitro*-m-*xylene*, m. p. 86·5°, and ω-4-*dinitro*-m-*xylene*, m. p. 64°.
F. M. G. M.

Preparation of Chloroalkylarylsulphonic Acids and of Chloroalkylarylcarboxylic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 239311).—ω-*Chlorotoluene*-p-*sulphonic acid* is readily prepared by slowly dropping water (18 parts) into ω-chlorotoluene-*p*-sulphonyl chloride (225 parts) dissolved in 80 parts of hot alcohol. The *sodium* salt, $SO_3Na\cdot C_6H_4\cdot CH_2Cl$, is sparingly soluble in water.

ω-*Dichlorotoluene*-m-*sulphonyl chloride*, a crystalline powder insoluble in water and prepared by the action of phosphorus pentachloride on benzaldehyde-*m*-sulphonic acid, is converted by the foregoing treatment into ω-*dichlorotoluene*-m-*sulphonic acid*; the *sodium* salt is moderately soluble in water.

ω-*Chloro*-p-*toluoyl chloride*, a colourless oil, b. p. 150—155° (prepared by chlorinating a hot solution of *p*-toluoyl chloride), when dissolved and maintained at 0—5° in 98% sulphuric acid until the evolution of hydrogen chloride ceases, furnishes ω-*chloro*-p-*toluic acid*, m. p. 190—192° (decomp.), and insoluble in water.
F. M. G. M.

Preparation of Aromatic Sulphonyl Ammonium Compounds. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 239763).—When sodium ω-chlorotoluene-*p*-sulphonate is heated with dimethylaniline at 70°, it yields the *compound*, $C_6H_4{<}{CH_2 \atop SO_3}{>}NMePh$, a colourless powder.

Ethyl ω-2-*dichlorotoluene*-p-*sulphonate*, a colourless oil prepared by hydrolysing the corresponding sulphonyl chloride with sodium ethoxide, when similarly treated furnishes the *compound*,

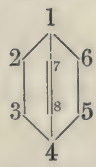
$$SO_3Et\cdot C_6H_3Cl\cdot CH_2\cdot NClMe_2Ph,$$

in colourless, hygroscopic crystals readily soluble in water and alcohol.
F. M. G. M.

System of Nomenclature for "Bridged Rings." Victor Grignard (*Bull. Soc. chim.*, 1912, [iv], 11, 124—129).—The author proposes to avoid the inconveniences of von Baeyer's system of nomenclature for such structures by (1) selecting for the nucleus of the name that of the fundamental ring, which is immediately apparent, traversed by one or more bridges; (2) numbering the atoms in the bridges, after those of the fundamental ring, so that the bridges appear to be merely particular substituents attached at two points, and identified in the name by their "characteristic." This characteristic consists of the numbers of all the atoms, which appear in the "bridge," and the highest number in it indicates the total number of carbon atoms in the structure. The number of constituent rings, apart from the fundamental ring, is always twice the number of bridges, and is indicated by prefixes, bicyclo, tetracyclo, etc. Where the bridge contains an ethylenic linking, these prefixes become bicycleno and tetracycleno respectively, and the number of the atom at which the double linking begins is accented in the "characteristic." The following examples of the application of the system may be given:

Bicyclo-(1 : 4)-hexane.

Tetracyclo-$\begin{bmatrix}1:7:4\\2:6\end{bmatrix}$-hexane.



Bicycleno-(1 : 7′ : 8 : 4)-hexane.

T. A. H.

Compounds of Antimony Trichloride and Tribromide with Polynuclear Benzene Hydrocarbons. Boris N. Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1805—1820).—Diphenyl and diphenylmethane form with antimony trihalides molecular compounds containing 2 mols. of antimony salt to 1 mol. of hydrocarbon: $2SbCl_3,C_6H_5Ph$, m. p. 71°; $2SbBr_3,C_6H_5Ph$, 60·5°; $2SbI_3,C_6H_5Ph$, 161°; $2SbCl_3,CH_2Ph_2$, m. p. 100°; $2SbBr_3,CH_2Ph_2$, m. p. 90°. Each concentration-temperature diagram exhibits two eutectic points, as follows:

System.	M.p. Hydro-carbon.	1st eutectic point. Tempera-ture.	1st eutectic point. *n*.	2nd eutectic point. Tempera-ture.	2nd eutectic point. *n*.	M. p. SbX_3.
$SbCl_3—C_6H_5Ph$	70·5°	50°	2·2	57°	0·18	73°
$SbBr_3—C_6H_5Ph$	70·5	47	1·75	60·5	0·52	94
$SbI_3—C_6H_5Ph$	70·5	68	89·4	160	0·2	166
$SbCl_3—CH_2Ph_2$	26	22·5	15·6	67	0·6	73
$SbBr_3—CH_2Ph_2$	26	22·5	14·6	82	0·18	94

With antimony trichloride and tri-iodide, diphenyl gives stable compounds, which melt without decomposing, whilst with antimony tribromide it yields a compound with a melting point in the region of unstable equilibrium.

Triphenylmethane forms no molecular compound with antimony tribromide, but with the trichloride it gives the compound $SbCl_3,CHPh_3$, melting at 49·5° in the region of unstable equilibrium. The diagram consists of three branches, the first eutectic point, corresponding with $SbCl_3,0{\cdot}93CHPh_3$, lying at 49°, and the second with $SbCl_3,0{\cdot}37CHPh_3$, at 35°.

The diminished capacity to form compounds with antimony trihalides observed in the case of triphenylmethane may be related to the fact that this hydrocarbon differs considerably in its chemical properties from diphenylmethane; thus, it forms molecular compounds with benzene and other hydrocarbons, and yields metallic derivatives, etc.

Colorations are often observed on fusing these polynuclear hydrocarbons with antimony trihalides (compare Watson Smith, Abstr., 1879, 831). T. H. P.

Halogen Derivatives of Fluorene and Bisdiphenylene-ethylene. JULIUS SCHMIDT and HANS WAGNER (*Annalen*, 1912, **387**, 147—164).—The method of converting 9 : 9-dichlorofluorene into bisdiphenylene-ethylene by heating with copper powder in benzene (Abstr., 1910, i, 550) has been applied to other halogenated fluorene derivatives; thus 9 : 9-*dichloro-2-bromofluorene*, $\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_4\end{array}\!\!>CCl_2$, m. p. 178°, colourless needles, obtained from 2-bromofluorenone and phosphorus pentachloride at 160—180°, is converted into 2 : 2′-*dibromobisdiphenylene-ethylene*, $\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_4\end{array}\!\!>C{:}C<\!\!\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_4\end{array}$, m. p. 312°, red crystals, or, by sublimation, yellowish-green needles. This substance is converted into 2 : 2′-*dibromobisdiphenylene-ethane*,

$$\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_4\end{array}\!\!>CH{\cdot}CH<\!\!\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_4\end{array},$$

m. p. 272°, colourless needles, by heating its ethereal solution with platinum black for eight hours in a current of hydrogen, and reacts additively with chlorine in chloroform and with bromine in carbon disulphide in sunlight to form respectively 9 : 9′-*dichloro*-2 : 2′-*dibromobisdiphenylene-ethane*, $\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_4\end{array}\!\!>CCl{\cdot}CCl<\!\!\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_4\end{array}$, m. p. 268°, colourless crystals, and 2 : 2′ : 9 : 9′-*tetrabromobisdiphenylene-ethane*, m. p. 258°; the latter in benzene reacts with silver acetate to form the *diacetate*, $\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_4\end{array}\!\!>C(OAc){\cdot}C(OAc)<\!\!\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_4\end{array}$, m. p. 285°.

9 : 9-*Dichloro*-2 : 7-*dibromofluorene*, $\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_3Br\end{array}\!\!>CCl_2$, m. p. 260°, colourless needles, obtained from 2 : 7-dibromofluorenone and phosphorus pentachloride at 210—220°, is converted by copper into 2 : 2′ : 7 : 7′-*tetrabromobisdiphenylene-ethylene*, $\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_3Br\end{array}\!\!>C{:}C<\!\!\begin{array}{l}C_6H_3Br\\ \vert\\ C_6H_3Br\end{array}$, m. p. 364°, red crystals, from which the following substances have been prepared: 9 : 9′-*dichloro*-2 : 2′ : 7 : 7′-*tetrabromobisdiphenylene-ethane*, m. p. 298—299°,

colourless needles; 2 : 2′ : 7 : 7′ : 9 : 9′-*hexabromobisdiphenylene-ethane*, m. p. 310°, colourless crystals; 2 : 2′ : 7 : 7′-*tetrabromobisdiphenylene-ethane*, m. p. 284°, colourless leaflets. The disappearance of colour coincidently with that of the ethylenic linking is noteworthy.

When heated in a sealed tube at 180° for six hours, fluorenone and phosphorus pentachloride yield 9 : 9′-*dichlorobisdiphenylene-ethane*, m. p. 235—236°, 2 : 7 : 9 : 9-*tetrachlorofluorene*, m. p. 215°, and a little 2 : 7-*dichlorofluorenone* (?), m. p. 187—189°. 2 : 7-Dichlorofluorenone, m. p. 185—186° (which appears to be identical with Goldschmiedt and Schranzhofer's β-dichlorofluorenone), is obtained best by heating 2 : 7-dinitrofluorenone with phosphorus pentachloride in a sealed tube at 170—180°, and boiling the resulting 2 : 7 : 9 : 9-tetrachlorofluorene with water; it forms an *oxime*, decomp. 243°, *phenylhydrazone*, decomp. 186—187°, and *semicarbazone*, decomp. 345°, and is converted by copper into 2 : 2′ : 7 : 7′-*tetrachlorobisdiphenylene-ethylene*, a red substance, m. p. above 380°. C. S.

The Preparation and Reactions of Bis-α-hydrindone-(2 : 2-)-spiran. HERMANN LEUCHS and DAN RADULESCU (*Ber.*, 1912, 45, 189—201).—Dibenzylmalonic acid, the preparation of which is fully described, is converted, by means of phosphorus pentachloride, into *dibenzylmalonyl chloride*, b. p. 216—218°/17 mm., 232—235°/32 mm., m. p. 68—69°. When dissolved in ether and treated with ammonia and aniline respectively, this yields the corresponding *amide* (m. p. 198—199°) and *anilide* (m. p. 196—197°). Boiling alcohol converts it into the *ester*. During distillation of the chloride under diminished pressure, as also when it is heated at 250—270° for some time, hydrogen chloride is evolved, and small quantities of *bis-α-hydrindone-(2 : 2-)spiran* formed. The latter is best prepared by distilling the chloride under diminished pressure in the presence of 2% of aluminium chloride. It has b. p. 255—257°/12 mm. (corr.), m. p. 174°. Phenylhydrazine converts it into *bis-α-hydrindone-(2 : 2-)-spiranbisphenylhydrazone*, colourless prisms, m. p. 200—201° (decomp.). When treated with hydroxylamine, a *substance*, $C_{17}H_{13}O_2N$, is formed (m. p. 214—215°), which possibly has the formula

$$C_6H_4<\begin{matrix}CH_2\\CO\cdot NH\end{matrix}>C<\begin{matrix}CH_2\\CO\end{matrix}>C_6H_4.$$

Under the action of sodium hydroxide, bis-α-hydrindone-(2 : 2-)-spiran readily yields the *sodium* salt of a strong, monobasic acid, which is stable towards excess of alkali. The free *acid* has m. p. 140—142°, and, when heated at 220°, evolves water vapour with the reformation of spiran. The composition of the acid is probably expressed by the formula $C_6H_4<\begin{matrix}CH_2\\CO_2H\end{matrix}\diagdown HC<\begin{matrix}CH_2\\CO\end{matrix}>C_6H_4.$

It can be resolved into optically active forms by crystallisation of the brucine salt from acetone. Attempts were made to prepare the *methyl* ester of the acid by the action of methyl iodide on the *silver* salt. The ester could not be obtained in the crystalline state. When distilled under diminished pressure, it decomposed with the regeneration of spiran.

Bis-α-hydrindone-(2 : 2-)-spiran, when treated with alcoholic ammonia,

forms two *compounds*, $C_{17}H_{13}ON$, m. p. 246—248° (decomp.), and $C_{17}H_{15}O_2N$. The latter, when rapidly heated, melts at 124—128° (decomp.), and is readily transformed into the former by heating it above its m. p., or by treating it with concentrated hydrochloric acid. These substances are probably not the nitrile and amide of the above-described acid, since neither evolves ammonia when treated with potassium hydroxide. The following formulæ are provisionally proposed for them: $C_6H_4<\begin{matrix}-CH_2-\\CH{:}N\end{matrix}>C<\begin{matrix}CH_2\\CO-\end{matrix}>C_6H_4$ and

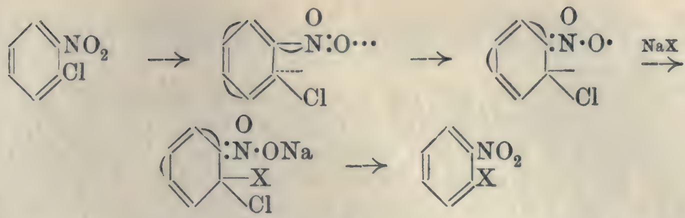
$$C_6H_4<\begin{matrix}\text{——}CH_2\text{——}\\CH(OH)\cdot NH\end{matrix}>CH<\begin{matrix}CH_2\\CO-\end{matrix}>C_6H_4.$$

Anhydrobis-a-hydrindonespiran, obtained in small quantity by the distillation of dibenzylmalonyl chloride under ordinary pressure in the presence of 4% of aluminium chloride, crystallises from glacial acetic acid in light red needles, m. p. 256—257°. H. W.

Reactivity of Side-chains in Nuclear Nitrated Homologues of Benzene. WALTHER BORSCHE (*Annalen*, 1912, **386**, 351—373).—One of the halogen atoms is readily substituted, the other only with difficulty, when 1 : 3-dichloro-4 : 6-dinitrobenzene is warmed in ether with an excess of ethyl sodioacetoacetate. On the other hand, both methyl groups react readily when 4 : 6-dinitro-*m*-xylene and benzaldehyde (2 mols.) are heated at 190° with a little piperidine; the main product is 4 : 6-*dinitro*-1 : 3-*distyrylbenzene*,

$$C_6H_2(NO_2)_2(CH{:}CHPh)_2,$$

m. p. 186°, yellow needles, very little 4 : 6-*dinitro*-3-*methylstilbene*, $C_6H_2Me(NO_2)_2\cdot CH{:}CHPh$, m. p. 145°, being formed. Trinitromesitylene, dinitromesitylene, trinitro-ψ-cumene, and 2 : 4-dinitroethylbenzene do not react with benzaldehyde. 2 : 4 : 6-Trinitrotoluene yields trinitrostilbene (Ullmann and Gschwind, Abstr., 1908, i, 622). 2 : 4 : 6-Trinitro-*m*-xylene, benzaldehyde, and a little piperidine, when heated in boiling amyl alcoholic solution, yield 2 : 4 : 6-*trinitro*-1 : 3-*distyrylbenzene*, $C_{22}H_{15}O_6N_3$, m. p. 147—148°, yellow needles. Corresponding *substances*, $C_{24}H_{19}O_8N_3$, m. p. 155°, and $C_{22}H_{13}O_{10}N_5$, m. p. 268° (decomp.), are obtained with anisaldehyde and *p*-nitrobenzaldehyde respectively. These condensations proceed most smoothly in the toluene series, less readily in the xylene series, and badly or not at all in the mesitylene series. The author is of opinion that in these nitrated methylbenzenes the distribution of the residual affinity of the benzene nucleus is such that, when only one methyl group is present, the influence of the residual affinity is concentrated on the carbon atom of this methyl group, its hydrogen atoms, therefore, becoming more mobile; as, however, the symmetry of the whole molecule is increased by the introduction of two and three methyl groups, the influence of the residual affinity is distributed between the methyl groups, with the result that their hydrogen atoms become less and less mobile. In the case of the chloronitrobenzenes, the elimination of the halogen atom is due, according to the author, not to any weakening of the union between it and the carbon atom, but rather to a striving of the molecule to assume an ortho- or para-quinonoid structure; the reagent s then held additively, the final product being obtained by the elimination of a halide; thus:



Ullmann and Gschwind (*loc. cit.*) have shown that the reactivity of the methyl group in 2 : 4-dinitrotoluene still persists when one of the nitro-groups is replaced by a carboxylic, sulphonic, or cyanogen group. The author finds, however, that in 6-nitro-4-cyano-*m*-xylene only one methyl group reacts with benzaldehyde and a little piperidine at 190—200°, giving a very poor yield of 6-*nitro*-4-*cyano*-3-*methylstilbene* (?), $NO_2·C_6H_2Me(CN)·CH\!:\!CHPh$, m. p. 183—184°, yellow needles. 2 : 4-Dicyanotoluene does not react with benzaldehyde.

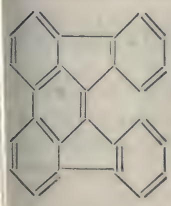
4 : 6-Dinitro-1 : 3-distyrylbenzene forms a *tetrabromide*,

$$C_6H_2(NO_2)_2(CHBr·CHPhBr)_2,$$

m. p. 207—208° (decomp.), and by reduction with stannous chloride and acetic and hydrochloric acids yields 4 : 6-*diamino*-1 : 3-*distyrylbenzene*, m. p. 204°, yellow crystals with green fluorescence. The base forms fluorescent solutions, yields a *dibenzoyl* derivative which is unchanged at 275°, and reacts with benzaldehyde in boiling alcohol to form the *dibenzylidene* derivative, $C_6H_2(N\!:\!CHPh)_2(CH\!:\!CHPh)_2$, m. p. 238—239°, deep yellow, non-fluorescent needles. A methyl-alcoholic solution of the base is reduced by hydrogen in the presence of a little colloidal palladium, yielding 4 : 6-*diamino*-1 : 3-*di*-β-*phenylethylbenzene*, $C_6H_2(NH_2)_2(CH_2·CH_2Ph)_2$ (*diacetyl* derivative, m. p. 224°; *dibenzoyl* derivative, m. p. 273°).

4-Cyano-*m*-xylene and nitric acid, D 1·52, at 0° yield a mixture of sparingly soluble (in alcohol), yellowish prisms, m. p. 107—108° (probably 6-*nitro*-4-*cyano*-m-*xylene*), and easily soluble, white needles, m. p. 120—121° (probably 4-*cyano*-2-*nitro*-m-*xylene*). By diazotisation and treatment with cuprous cyanide, 4-cyano-*o*-toluidine yields 2 : 4-*dicyanotoluene*, m. p. 144—145°, white needles. C. S.

Non-Existence of ψ-Diphenyleneketone [ψ-Fluorone]. A New Red Hydrocarbon. Rudolf Pummerer (*Ber.*, 1912, **45**, 294—298).—The red modification of fluorone, obtained by Kerp (Abstr., 1896, i, 238; compare also Stobbe, *ibid.*, 1911, i, 651) by the distillation of calcium diphenoxide, is shown to be the ordinary yellow variety of fluorone, contaminated with traces of the red substance, first observed by Fittig and Ostermayer (this Journ., 1873, 892), and shown by them to be produced simultaneously in the distillation. This red impurity is insoluble in alcohol and solvents of low b. p., but dissolves to a slight extent in solutions of fluorone, from which it may be removed by shaking in the cold with animal charcoal.



It may be isolated by repeatedly triturating the "red fluorone" with cold alcohol and crystallising the residue from benzene. It forms slender, lancet-shaped crystals, m. p. 306°, yields strongly

yellow, fluorescent solutions, and has the composition $C_{26}H_{14}$. On account of its bright red colour, the hydrocarbon is termed by the author *rubicene.*

Its constitution has not yet been definitely established, but arguments are advanced in favour of the formula given on the preceding page. With bromine in chloroform solution, it forms a *bromo*-substitution product; the *picrate* crystallises in very slender, brownish-red prisms.

Kerp's "red fluorone" contains in addition to rubicene a white substance, which remains behind on dissolving the ketone in concentrated sulphuric acid. F. B.

Isomeric Schiff's Bases. BRONISLAW PAWLEWSKI (*Chem. Zentr.*, 1912, i, 29; from *Chem. Polski*, 1911, **11**, 121—122).—Of the five substances obtained by the author by condensing benzoin with benzylamine, one, m. p. 88—90°, is the trans-modification of *benzylidenebenzylamine*, $CHPh\colon N\cdot CH_2Ph$, and is stereoisomeric therefore with the liquid benzylidenebenzylamine, b. p. 200—202°/10—20 mm., described by Mason and Winder (Trans., 1894, **65**, 191). C. S.

The Homo-chromoisomerism of the Phenylmethylpicramides. ARTHUR HANTZSCH (*Ber.*, 1912, **45**, 360—363).—Polemical; a reply to Biilmann (Abstr., 1911, i, 963). D. F. T.

Nitration of the Acyl Derivatives of *p*-Anisidine. FRÉDÉRIC REVERDIN and ARMAND DE LUC (*Ber.*, 1912, **45**, 349—354).—A continuation of earlier work (Abstr., 1909, i, 377, 913; 1910, i, 470), in which a study has been made of the effect of the substitution of the nitrobenzoyl group into the amino-group of *p*-anisidine on the behaviour of the base towards nitration.

m-*Nitrobenzenesulphonyl*-p-*anisidide*, $NO_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot OMe$, obtained by the action of the acid chloride on the base, forms white needles, m. p. 135°; the *acetyl* derivative forms needles, m. p. 181—182°.

o-*Nitrotoluene*-p-*sulphonyl*-p-*anisidide*, obtained similarly, forms needle crystals, m. p. 81°; *acetyl* derivative, m. p. 161°.

The nitration of the above nitrobenzenesulphonyl-*p*-anisidide with nitric acid, D 1·38, without cooling (max. temperature 36°), gives as chief product an orange-yellow *dinitro*-derivative, m. p. 170°, which can be hydrolysed to the corresponding free base, 2 : 5-dinitro-*p*-anisidine. If the temperature is allowed to rise to 62°, a mixture of the previous dinitro-compound with the isomeric 3 : 5-*dinitro*-compound, m. p. 165—166°, is obtained; this forms white needles, and hydrolyses to 3 : 5-dinitro-4-aminoanisole. If the mixture during nitration is heated over a free flame, there is obtained the *nitrobenzenesulphonyl* derivative of 2 : 3 : 6-trinitro-4-aminoanisole, which forms small, prismatic crystals, m. p. 189—190°.

When nitrated as an emulsion in acetic acid at 70° with nitric acid D 1·38, the main product is the above 3 : 5-dinitro-derivative.

With nitric acid, D 1·52, between 0° and 5°, the product consists of a mixture of the 2 : 5-dinitro- and the 2 : 3 : 6-trinitro-derivatives; at higher temperatures decomposition occurs; if the nitration with acid of this strength is performed at 5—10° in an emulsion in acetic acid,

a *mononitro*-derivative is obtained (yellow needles, m. p. 127°), which on hydrolysis gives 3-nitro-4-aminoanisole.

With nitric acid, D 1·38, the above-mentioned nitrotoluenesulphonyl-*p*-anisidide at 36° yields a *mononitro*-derivative (prismatic crystals, m. p. 132°), the constitution of which is shown by its hydrolysis to 3-nitro-*p*-anisidine. At higher temperatures, the *nitrotoluenesulphonyl* derivatives of 3 : 5-dinitro- and 2 : 3 : 6-trinitro-*p*-anisidine are obtained (m. p. 125—140° and 184—185° respectively); the former of these is also the product of nitrating a solution in acetic acid.

With nitric acid, D 1·52, at 5—10°, the product contains the *nitrotoluenesulphonyl* derivatives of 2 : 3-dinitro-*p*-anisidine and 2 : 5-dinitro-*p*-anisidine (m. p. of acyl derivatives, 180° and 154° respectively); on nitrating in acetic acid in the cold, the above-mentioned nitrotoluenesulphonyl derivatives of 3-nitro-*p*-anisidine and 2 : 5-dinitro-*p*-anisidine are obtained, the latter preponderating.

D. F. T.

Decomposition of Mixed Phenyl Oxides in Presence of Nickel and Hydrogen. ALPHONSE MAILHE and M. MURAT (*Bull. Soc. chim.*, 1912, [iv], 11, 122—123).—It is shown that all phenyl alkyl oxides when passed over heated nickel in a current of hydrogen are decomposed in accordance with the equations (1) $C_6H_5{\cdot}O{\cdot}R + H_2 = C_6H_5{\cdot}OH + RH$, and (2) $C_6H_5{\cdot}O{\cdot}R + H_2 = C_6H_6 + R{\cdot}OH$, the alcohol and the paraffinic hydrocarbon formed being destroyed by the further action of the nickel. Anisole is most readily attacked, and yields 52% of the possible weight of phenol, whilst phenyl *iso*amyl oxide yields only 22%. Diphenyl oxide is attacked with great difficulty, and gives only 6% of the possible weight of phenol. Veratrole at 205° yields 16% of the possible weight of guaiacol, and the latter, on further treatment at 205°, yields a mixture of phenol and catechol.

T. A. H.

[Preparation of *p*-Aminophenyl Methyl Mercaptole.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 239310).—p-*Aminophenyl methyl mercaptole*, a colourless oil, comparing favourably with phenacetin in therapeutical action, is obtained by reducing *p*-nitrophenyl methyl mercaptole (Blanksma, Abstr., 1902, i, 281); the salts are colourless and crystalline, and the *acetyl* derivative forms colourless needles, m. p. 127—128°.

F. M. G. M.

Preparation of 4-Chloro-α-naphthol. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 240038).—It is found that 4-chloro-α-naphthol can be prepared by treating α-naphthol arylsulphonyl ethers with chlorinating agents. α-*Naphthyl* p-*toluenesulphonate*, colourless needles, m. p. 83—84°, prepared by the action of *p*-toluenesulphonyl chloride on sodium α-naphthoxide in alcoholic solution, was dissolved in carbon tetrachloride and treated with chlorine, when a satisfactory yield of 4-chloro-α-naphthol (m. p. 116°) was obtained.

F. M. G. M.

The Red Coloration Produced in the Ferric Chloride Reaction with Catechol in Alkaline Solution. I. RUDOLF FRIEDRICH WEINLAND and KARL BINDER (*Ber.*, 1912, 45, 148—154).—The green coloration of an aqueous catechol solution produced by ferric chloride is changed to deep red on the addition of sodium, potassium, ammonium, barium, calcium, and magnesium hydroxides. The red coloration is due to the formation of salts of an acid,

$$H_3[Fe'''(C_6H_4O_2)_3],$$

analogous to the ferricyanides or ferrioxalates.

The *potassium* salt, $K_3[Fe'''(C_6H_4O_2)_3],2H_2O$, is obtained as a lustrous, crystalline, brownish-black to dark bronze-red powder, consisting of microscopic triangular prisms, by the addition of ferric acetate to a solution of catechol in strong aqueous potassium hydroxide. It readily dissolves in water to deep red solutions, which are decolorised by excess of acid with the liberation of catechol. When heated with sodium sulphide or potassium cyanide in aqueous solution, the potassium salt is decomposed, yielding ferrous sulphide and potassium ferrocyanide respectively, although in the presence of potassium hydroxide the aqueous solutions may be heated with the substances without undergoing change.

The tendency to form salts of the above acid is so pronounced, that freshly precipitated ferric hydroxide in the presence of aqueous alkalis or ammonia dissolves on the addition of catechol, forming the corresponding alkali or ammonium salt.

The *ammonium* salt, $(NH_4)_3[Fe'''(C_6H_4O_2)_3],H_2O$, prepared in a similar manner to the sodium salt, is a brownish-black powder, consisting of microscopic, flat, violet-red needles.

The *sodium* salt, $Na_3[Fe'''(C_6H_4O_2)_3],10H_2O$, forms microscopic, red, hexagonal columns, capped with truncated pyramids.

The *lead* salt is precipitated quantitatively on the addition of lead acetate to an aqueous solution of an alkali salt. The *morphine* and *strychnine* salts are crystalline; the *quinine* and *brucine* salts are amorphous.

Similar complex salts, stable towards alkalis, are obtained from catechol and aluminium, cupric, nickel, cobalt, and manganous salts, and also from pyrogallol, salicylic, gallic or protocatechuic acids, and ferric salts in alkaline solution. F. B.

Derivatives of 4-Amino-orcinol (2-Amino-3:5-dihydroxytoluene). FERDINAND HENRICH, G. TAUBERT, and H. BIRKNER (*Ber.*, 1912, 45, 303—314. Compare Abstr., 1903, i, 413).—2-Amino-orcinol has now been isolated in the free condition by the addition of sodium hydroxide to a cold aqueous solution of the hydrochloride in quantity just insufficient for complete decomposition. It crystallises from ethyl acetate in lustrous, silvery-white leaflets, decomposing at 188—190°, with previous darkening at 160—180°. Its hydrochloride is oxidised by chromic acid in aqueous solution to 4-*chloro-3-hydroxytoluquinone*, $CO<\begin{matrix}CCl:C(OH)\\CH{=\!=}CMe\end{matrix}>CO$, which forms intensely yellow crystals, m. p. 181—182°, volatile in ether vapour, dissolves in alkalis, yielding intensely red solutions, and is reduced by

sulphur dioxide in aqueous solution to 4-*chloro*-2 : 3 : 5-*trihydroxytoluene*, $C_7H_7O_3Cl$, colourless needles, m. p. 137·5°. Acidification of the solutions of the quinone in aqueous ammonia or sodium carbonate results in formation of a *substance* having the same composition as the original quinone. This substance separates from benzene or chloroform in yellow crystals, darkening at 220°, dissolves in water less readily than the original quinone, and is not volatile in ether vapour; but whether these differences are to be referred to isomerism or polymerism has not yet been determined.

That the quinone has the above constitution and not that of the isomeric 6-chloro-3-hydroxytoluquinone, $CO<\begin{matrix}CH:C(OH)\\CCl=CMe\end{matrix}>CO$, has been established by the synthesis of the latter compound from 2-amino-orcinol hydrochloride. This is converted by amyl nitrite in alcoholic solution into *orcinol*-2-*diazonium chloride*, a yellowish-white powder, which forms, with cuprous chloride, a red, crystalline *additive* compound, $C_6H_2Me(OH)_2 \cdot N_2Cl,Cu_2Cl_2$. When heated under diminished pressure the additive compound melts at 80—90°, and decomposes at a higher temperature into 2-*chloro-orcinol*, $C_7H_7O_2Cl$, m. p. 138—139°, with previous sintering at 115°.

The last-named compound reacts with amyl nitrite and potassium hydroxide in alcoholic solution to form the *potassium* salt of 2-chloro-6-nitroso-orcinol, from which the free nitroso-compound is obtained by acidification with dilute sulphuric acid.

2-*Chloro*-6-*nitroso-orcinol*, $C_7H_6O_3NCl$, exists in two modifications: a stable, yellow, crystalline form, melting at 159—160° with previous darkening, and a brown modification, which passes into the yellow variety when heated.

2-*Chloro*-6-*amino-orcinol hydrochloride* is obtained in slender, white needles by reducing the preceding nitroso-compound with stannous chloride and hydrochloric acid. It is oxidised by chromic acid in aqueous solution to 6-*chloro*-3-*hydroxytoluene*, ruby-red crystals, m. p. 165—166° (decomp.). F. B.

Constitution of Di*iso*eugenol. ERNESTO PUXEDDU (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 42—46. Compare Abstr., 1909, i, 225).—The paper deals with the action of light on *iso*eugenol and on its methyl, ethyl, and propyl ethers, as well as the action of light on eugenol and its ethers. The author has also examined the action of nitrous acid on *iso*eugenol ethyl ether and on di*iso*eugenol diethyl ether.

When a solution of 100 grams of *iso*eugenol in 200 c.c. of alcohol is treated with 25 c.c. of hydrochloric acid and exposed to light in a sealed tube, crystals of di*iso*eugenol are quickly deposited, and if the precipitate is collected after two days, the yield amounts to 60%. If the filtered solution is again exposed to light, a further quantity of the polymeride can be obtained. The mother liquors show a splendid blue fluorescence. Under the same conditions, sulphuric acid also acts feebly as a polymerising agent. *iso*Eugenol methyl ether, *iso*eugenol ethyl ether, and *iso*eugenol propyl ether yield the analogous *polymerides* when treated in the same way. iso*Eugenol propyl ether*, $C_{13}H_{18}O_2$,

prepared from *iso*eugenol with sodium propoxide and propyl iodide, crystallises in long, prismatic needles, m. p. 54°. *Diisoeugenol dipropyl ether*, $(C_{13}H_{18}O_2)_2$, forms prismatic needles, m. p. 94°.

Eugenol and its methyl and ethyl ethers under the same conditions are not acted on by light.

When *iso*eugenol ethyl ether is treated with glacial acetic acid and potassium nitrite, a substance, $C_{12}H_{14}O_4N_2$, is obtained, which crystallises in yellow, tabular prisms, m. p. 85°. It is assigned the formula of the *peroxide*,

$$\begin{array}{l} C_6H_3(OMe)(OEt)\cdot C{=\!=}N\cdot O, \\ \qquad\qquad\qquad\qquad\quad CMe{:}N\cdot O \end{array}$$

analogous to that from *iso*eugenol methyl ether (compare Malagnini, Abstr., 1895, i, 35). Di*iso*eugenol diethyl ether does not react with nitrous acid, and therefore probably does not contain an unsaturated side-chain. R. V. S.

Action of Phorone on Catechol and Pyrogallol. Mario Ghiglieno (*Atti R. Accad. Sci. Torino*, 1912, **47**, 16—22).—Fabinyi and Széki (compare Abstr., 1905, i, 591, 888) obtained products by heating acetone with catechol and with pyrogallol in a sealed tube at 145°. In the present paper it is shown that the formulæ ascribed to these substances are incorrect. Under the conditions of experiment the acetone is condensed to phorone, which reacts with the phenols, giving substances of the following constitutions, respectively:

$$C(CH{:}CMe_2)_2[C_6H_3(OH)_2]_2$$

and $C(CH{:}CMe_2)_2[C_6H_2(OH)_3]_2$. This explains the existence of the tetrabromo- and dibromo-derivatives. In confirmation of this view, the authors have prepared the same substances, using phorone instead of acetone. It is not necessary to heat the mixture at 145°; the same products are obtained when phorone and the phenol are heated together in a sealed tube at 100°, or even in an open flask with condenser. In the case of the product from pyrogallol the somewhat discordant analyses of Fabinyi and Széki are explained by the fact that the substance contains 1 mol. H_2O, which it loses completely only at 130—140°, and which it re-absorbs very readily on exposure to air. R. V. S.

Action of Formic Acid on Triarylcarbinols. Alfred Guyot and A. Kovache (*Compt. rend.*, 1912, **154**, 121—122).—Triarylcarbinols are readily reduced when treated with twenty times their weight of crystallisable formic acid, giving the corresponding hydrocarbons with formation of water and evolution of carbon dioxide. The reaction may be made use of for accurately determining the number of hydroxyl groups in such carbinols, by weighing the carbon dioxide evolved from less than a gram of the substance. Quantitative results were obtained with triphenylcarbinol, phenyldi-*p*-tolylcarbinol, *o*-benzoyltriphenylcarbinol, and 9 : 10-diphenylanthranol, whilst 9-phenylanthranol and 9 : 10-dihydroxy-9 : 10 : 10-triphenyldihydroanthracene gave less than the calculated amount of carbon dioxide, although the yield of hydrocarbon was theoretical. W. O. W.

The Walden Inversion and Substitution Processes. EMIL FISCHER (*Annalen*, 1912, 386, 374—386. Compare Abstr., 1911, i, 418).—An amplification of the author's view that the phenomena met with in the addition of halogens or halogen hydracids to stereoisomeric unsaturated compounds are probably of a similar type to the Walden inversion. Reactions such as that whereby both inactive dibromosuccinic acids result by the addition of bromine to maleic or to fumaric acid have been regarded by Werner and by van't Hoff as exceptional and due to a specific action of the halogen. Examples are given, however, to show that similar results may be obtained by the addition of groups or atoms other than halogens. It is true that the oxidation of cinnamamide by potassium permanganate yields only one *phenylglyceramide*, $OH\cdot CHPh\cdot CH(OH)\cdot CO\cdot NH_2$, m. p. 161—162° (corr.) (which yields the phenylglyceric acid, having m. p. 141°, by hydrolysis), and the oxidation of cinnamoylglycine gives only one *phenylglycerylglycine*, $OH\cdot CHPh\cdot CH(OH)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 144—145° (corr.). However, Baeyer has shown that Δ^1-tetrahydrophthalic acid yields two stereoisomeric hexahydrophthalic acids by reduction, whilst Fittig has obtained two dimethylsuccinic acids by the reduction of dimethylfumaric acid.

C. S.

Spectrochemical Differentiation between Hydroaromatic Compounds with Endocyclic and with Semicyclic Double Linkings. KARL AUWERS and PHILIPP ELLINGER (*Annalen*, 1912, 387, 200—239).—Unsaturated hydroaromatic hydrocarbons containing semicyclic double linkings exhibit a moderate exaltation of the specific refraction and a marked exaltation of the specific dispersion. Unsaturated hydroaromatic hydrocarbons containing endocyclic double linkings are optically normal. These statements are based, not only on the spectrometric examination of the many alkylidene*cyclo*paraffins which have been prepared by Wallach, but also on a direct comparison of the alkylidene*cyclo*hexanes (methylene-, ethylidene-, and *iso*propylidene-*cyclo*hexanes) with the isomeric alkyl-Δ^1-*cyclo*hexenes (methyl-, ethyl-, and *iso*propyl-*cyclo*hexenes); the latter are optically normal, whilst the former exhibit an exaltation of 0·28—0·47 of Σ_D, and an exaltation of 6—10% of $\Sigma_\gamma - \Sigma_\alpha$.

The spectrochemical method of differentiating between the two classes of isomerides has been utilised to show that Sabatier and Mailhe's alkylidene*cyclo*hexane derivatives are really unsaturated endocyclic compounds, and that Zelinsky and Gutt's 3-methyl-1-ethylidene*cyclo*hexane must be, on account of its optical normality, 3-methyl-1-ethyl-Δ^1-*cyclo*hexene.

Δ^1-*cyclo*Hexenylacetic acid and its esters and their homologues containing a methyl group in position α, 2, 3, or 4 are optically normal. *cyclo*Hexylideneacetic acid and its homologues containing a methyl group in position 2, 3, or 4 have too high m. p.'s to be suitable for spectrometric examination, but their methyl and ethyl esters show a marked exaltation, 0·79—1·05, of the specific refraction, Σ_D, and still more pronounced exaltation, 31—40%, of the specific dispersion, $\Sigma_\gamma - \Sigma_\alpha$. These are due, not only to the semicyclic, but also to the conjugated, double linking. Esters of the acids contain-

ing a methyl group in the α-position contain a disturbed conjugation, and therefore show smaller exaltations, but even in these cases the exaltations are so pronounced that there can be no uncertainty in distinguishing such esters from those of α-substituted *cyclo*hexenylacetic acids.

The authors regard the spectrometric method as far safer than any chemical process for the determination of the constitution of such easily changeable substances as *cyclo*hexenyl- and the *cyclo*hexylideneacetic acids.

The following new compounds are described; they have been obtained by Wallach's methods as a rule. 1-iso*Propyl*cyclo*hexanol*, $C_9H_{18}O$, b. p. 176·4—176·7°, $D_4^{15\cdot5}$ 0·9142, n_α 1·46064, n_D 1·46419, and n_γ 1·47387 at 15·5°; *ethyl* Δ^1-cyclo*hexenylacetate*, $C_6H_9{\cdot}CH_2{\cdot}CO_2Et$, b. p. 100°/12 mm., $D_4^{16\cdot2}$ 0·9829, n_α 1·46422, n_D 1·46906, n_γ 1·48017 at 16·2°; *methyl* α-1-*hydroxy*cyclo*hexylpropionate*,

$$OH{\cdot}C_6H_{10}{\cdot}CHMe{\cdot}CO_2Me,$$

b. p. 132°/18 mm., D_4^{20} 1·0537; *methyl* α-Δ'-cyclo*hexenylpropionate*, $C_6H_9{\cdot}CHMe{\cdot}CO_2Me$, b. p. 108—108·5°/18 mm., $D_4^{18\cdot3}$ 0·9864, n_α 1·46373, n_D 1·46648, n_γ 1·47885 at 18·3°; *methyl* 2-*methyl*cyclo*hexylideneacetate*, $C_6H_9Me{:}CH{\cdot}CO_2Me$ (prepared from methyl iodide and the silver salt of the *acid*, m. p. 68°), b. p. 119·9°/15 mm., $D_4^{14\cdot2}$ 0·9767, n_α 1·47681, n_D 1·48072, n_γ 1·49802 at 14·2°; the corresponding *ethyl* ester has b. p. 128·2°/13 mm., $D_4^{14\cdot8}$ 0·9587, n_α 1·47524, n_D 1·47906, and n_γ 1·49639 at 14·8°; *methyl* 3-*methyl*cyclo*hexylideneacetate*, $C_6H_9Me{:}CH{\cdot}CO_2Me$, b. p. 117°/13 mm., $D_4^{15\cdot5}$ 0·9752, n_α 1·47534, n_D 1·47926, n_γ 1·49668 at 15·5°; the *ethyl* ester has b. p. 131·4°/18 mm., D_4^{15} 0·9571, n_α 1·47347, n_D 1·47730, n_γ 1·49464 at 15°.

C. S.

Correlation of Ionisation and Structure. II. Negatively Substituted Benzoic Acids. C. G. DERICK (*J. Amer. Chem. Soc.*, 1912, **34**, 74—82).—It was shown in an earlier paper (Abstr., 1911, ii, 713) that the free energy of ionisation for negatively substituted monobasic fatty acids in aqueous solution at 25° is the sum of the separate effects of each atom in the molecule. Hence it was demonstrated that the position of a negative atom or group in an acid can be determined if its α-"place factor" and the ionisation constant of the substituted acid are known. In the present paper it is shown that the additive relationship in the free energy of ionisation is also true in the case of aromatic acids, and that it is therefore possible to determine the structure of substituted benzoic acids containing negative groups or atoms, if the ortho-, meta-, and para-"place factors" are known for each negative radicle.

The "place factors" have been determined for benzoic acid for the acetoxy-, carboxy-, chloro-, hydroxy-, and nitro-radicles for the ortho-, meta-, and para-positions; for the aldehydo-, benzoyl-, bromo-, carbmethoxy-, carbethoxy-, iodo-, and methoxy-radicles for the ortho-position; and for the cyano-, fluoro-, and iodo-radicles for the meta-position. From these numbers the ionisation constants for the substituted benzoic acids were calculated, and agreed closely with the experimental values in nearly all cases.

There is no simple relation between the "place factors" for the same radicle substituted in the ortho-, meta-, and para-positions in benzoic acid. Ionisation will not differentiate between 2 : 3- and 2 : 5-di-substituted benzoic acids, in which the substituting radicles in the 3- and 5-positions are the same and those in the 2-positions are also the same. The fact that the 3- and 5-positions are equivalent with respect to the 1-position has been proved in terms of the free energy of ionisation. E. G.

Barium Hippurate. EYVIND BÖDTKER (*Chem. Zeit.*, 1912, **36**, 105).—Analyses of this salt, prepared by neutralising hippuric acid with barium hydroxide, crystallising it from water, and drying the crystals between blotting paper, show that it contains $5H_2O$. The statement that it contains only $1H_2O$ may be due to the salt having been dried over sulphuric acid before analysis, although the strontium salt, when similarly dried, does not lose water. Attempts to prepare ferric hippurate were not successful. W. P. S.

Preparation of Cinnamic Esters of Polyatomic Alcohols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 239650. Compare Abstr., 1911, i, 858).—*β-Chloroethyl cinnamate*, $CHPh:CH\cdot CO_2\cdot C_2H_4Cl$, a colourless solid, m. p. 31°, b. p. 188—191°/20 mm., is prepared by the interaction of chloroethyl alcohol and cinnamic acid in the presence of concentrated sulphuric acid; when heated at 140° with sodium acetate and dilute acetic acid, it furnishes *glycol cinnamate*, b. p. 170—175°/15 mm.

γ-Chloro-β-hydroxypropyl cinnamate,

$$CHPh:CH\cdot CO_2\cdot CH_2\cdot CH(OH)\cdot CH_2Cl,$$

a yellowish, viscid liquid, b. p. 210—218°/20 mm., prepared from monochlorohydrin and cinnamic acid, by similar treatment yields *glycerol cinnamate*. Other weak acids and their salts can replace acetic acid in this reaction. F. M. G. M.

Sodium Phenyl Carbonate as Intermediate Product of Kolbe's Synthesis for Salicylic Acid. CARL H. SLUITER (*Ber.*, 1912, **45**, 59—62).—It has been asserted (de Bruyn and Tymstra, Abstr., 1905, i, 209; Tymstra, Abstr., 1905, i, 439) that under the conditions of Kolbe's process, sodium phenyl carbonate cannot be an intermediate step on account of its dissociation into carbon dioxide and sodium phenoxide; in their opinion the carbon dioxide molecule inserts itself directly between the carbon and hydrogen atoms in the ortho-position of the sodium phenoxide, giving the phenolic sodium derivative of salicylic acid.

The author takes diphenyl carbonate (m. p. 78·2—78·4°, D^{14} 1·272, D^{100} 1·1032), and examines carefully the reaction products obtained by heating to 160° with an equimolecular quantity of dry sodium hydroxide (compare Hentschel, Abstr., 1883, 588) in a current of nitrogen. The evolution of carbon dioxide ends after two to three minutes, and the residue contains sodium phenoxide, sodium carbonate, and sodium salicylate with some unchanged diphenyl carbonate. Two reactions are, therefore, believed to occur concurrently:

(1) $PhO\cdot CO\cdot OPh + 2NaOH = 2PhOH + Na_2CO_3$;

(2) $PhO\cdot CO\cdot OPh + NaOH = Ph\cdot OH + PhO\cdot CO\cdot ONa$; the sodium phenyl carbonate then partly dissociates into carbon dioxide and sodium phenoxide, and partly is rearranged into sodium salicylate. The alternative explanation given above for the formation of the last substance cannot hold in this case, as the pressure of carbon dioxide would be quite insufficient for reaction with the sodium phenoxide. It appears, therefore, that under the conditions of Kolbe's synthesis, sodium phenyl carbonate can undergo rearrangement into sodium salicylate. D. F. T.

Two Phthaloximes and Some of Their Derivatives. WILLIAM R. ORNDORFF and DAVID S. PRATT (*Amer. Chem. J.*, 1912, **47**, 89—125). —It has been shown by R. Meyer (Abstr., 1905, i, 440; 1909, i, 652) that quinolphthalein yields three oximes, of which two are coloured, whilst the other is colourless. The coloured oximes,

$$O<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>C<\begin{matrix}C_6H_4\\O\end{matrix}>C{:}NOH,$$

were regarded as *cis-* and *trans*-stereoisomerides, and the group $C{:}NOH$ was considered to be the chromophore. In order to ascertain whether this group behaves as a chromophore when present in a five-membered ring, a study has been made of phthalylhydroxylamine, first described by Lassar-Cohn (Abstr., 1881, 585), which the authors prefer to term phthaloxime.

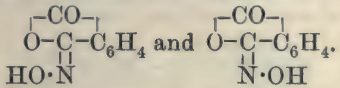
The compound was prepared by Lach's method (Abstr., 1883, 1104), which consists of heating a mixture of phthalic anhydride, hydroxylamine hydrochloride, sodium carbonate, and water for an hour at 60°. As the reaction product cooled, colourless crystals of phthaloxime separated, in quantity equivalent to a 70% yield. When the mother liquor was heated at 100° for one and a-half hours and then left to cool, lemon-yellow crystals of an isomeric phthaloxime appeared. These oximes, $C_6H_4<\begin{matrix}C({:}NOH)\\CO\end{matrix}>O$, both melt at 220—226°, and are slowly decomposed when heated at 110°. Both forms dissolve in alkali hydroxides with the production of red solutions, which gradually become colourless, owing to the formation of salts of the hydroxamic acid. If the colourless oxime is heated with a solvent containing a hydroxyl group, it is partly converted into the yellow isomeride, and, if boiled for an hour with glacial acetic acid, it is quantitatively transformed into the yellow form. The yellow oxime can be quantitatively changed into the colourless variety by boiling it with acetic anhydride, the same colourless *acetate*, m. p. 183—185°, being obtained in this case as when the colourless isomeride itself is acetylated. When the colourless acetate is treated with a solution of ammonia and afterwards acidified, the white oxime is precipitated. A yellow *acetate*, also of m. p. 183—185°, can be obtained from the yellow oxime by the action of acetic anhydride at the ordinary temperature.

Both oximes yield red *ammonium*, *sodium*, *sodium hydrogen*, *potassium hydrogen*, and *silver* salts, from which the original oxime is regenerated in each case on treatment with acids. When the silver salts are treated with ethyl iodide, that of the colourless oxime yields

a colourless *ethyl ether*, and that of the yellow oxime, a lemon-yellow *ethyl ether*, both melting at 95—100°.

Each oxime has been submitted to a crystallographic examination. The colourless oxime forms monoclinic needles, elongated in the direction of the *b*-axis, and usually flattened parallel to a pair of faces in the ortho-zone; the crystals have n_D 1·522 in a direction parallel to the elongation. The optical properties of the yellow oxime closely resemble those of the colourless form except in respect of colour. The colour of the yellow variety is due mostly, if not entirely, to fluorescence. A crystallographic study has also been made of the salts, acetates, and ethyl ethers.

The constitution of these oximes is discussed, and evidence is adduced to show that in all probability they are not structural isomerides, but stereoisomerides of the formulæ



E. G.

*iso*Phthalanil. RUDOLF PUMMERER and GUSTAV DORFMÜLLER (*Ber.*, 1912, **45**, 292—294).—The transformation of *iso*phthalanil into phthalanil, $\begin{matrix}CO\cdot O \\ | \\ C_6H_4\end{matrix}\!\!>C{:}NPh \longrightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NPh$, takes place slowly at the ordinary temperature, as indicated by the rise in m. p. of a specimen of the former compound from 116° to 150° after being kept for six months, and also by the isolation of phthalanil from the product. When shaken with concentrated aqueous sodium carbonate at the ordinary temperature, *iso*phthalanil undergoes complete transformation in the course of five hours. With dilute sodium carbonate it is converted, after several days, mainly into phthalanilic acid, only traces of phthalanil being produced; phthalanil undergoes no change when subjected to the same treatment. The transformation has also been effected by boiling solutions of *iso*phthalanil in pyridine, quinoline, and nitrobenzene; with water and light petroleum no change occurs.

*iso*Phthalanil reacts with benzene in the presence of aluminium chloride, yielding *o*-benzoylbenzanilide. F. B.

Simple Fatty Amines containing Sulphur. WILHELM SCHNEIDER (*Annalen*, 1912, **386**, 332—350).—The possibility that derivatives of aminosulphones, other than cheirolin (methyl-γ-thiocarbimidopropylsulphone) (Abstr., 1910, i, 658), may occur in nature has led the author to prepare aliphatic aminosulphones and the corresponding thiocarbimides, aliphatic aminosulphides, and aminosulphoxides.

[With MAX MÜLLER and WILHELM BECK.]—*β-Phthalimidoethyl methyl sulphide*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CH_2\cdot SMe$, m. p. 89°, prepared from sodium methyl mercaptide and β-bromoethylphthalimide, yields by hydrolysis *methyl β-aminoethyl sulphide*, $NH_2\cdot CH_2\cdot CH_2\cdot SMe$, b. p. 146—148°, a colourless liquid having the odour of piperidine and strongly basic properties (*hydrochloride*, m. p. about 120°; *picrate*, m. p. 119°; *picrolonate*, decomp. 187°; *oxalate*, m. p. 197°; *benzoyl*

derivative, m. p. 57°). By treatment with alkali and an excess of methyl iodide, it yields, not an *NS*-dimethiodide, as does methyl-γ-aminopropyl sulphide (*loc. cit.*), but the *methiodide* of methyl β-dimethylaminoethyl sulphide, $SMe\cdot CH_2\cdot CH_2\cdot NMe_3I$, decomp. 220·5°, colourless leaflets, which is decomposed by warm alkalis with evolution of trimethylamine.

β-Phthalimidodiethyl sulphide, $C_6H_4{<}{}^{CO}_{CO}{>}N\cdot CH_2\cdot CH_2\cdot SEt$, m. p. 39°, yields by hydrolysis *β-aminodiethyl sulphide*, $C_4H_{11}NS$, b. p. 163° (*hydrochloride*, m. p. 147°; *hydrogen oxalate*, m. p. 145·5°; *picrate*, m. p. 148°; *picrolonate*, decomp. 184°; *benzoyl* derivative, b. p. 221—222°/40 mm. [decomp.]). The *methiodide* of β-dimethylaminodiethyl sulphide decomposes at 216·5°.

By oxidising its hydrochloride with hydrogen peroxide and treating the product with alcoholic sodium ethoxide, methyl β-aminoethyl sulphide yields *methyl β-aminoethyl sulphoxide*,

$$CH_3\cdot SO\cdot CH_2\cdot CH_2\cdot NH_2,$$

which cannot be distilled, but is volatile with steam. It forms an *oxalate*, m. p. 165°, *picrate*, m. p. 158°, and *picrolonate*, decomp. 205°, and is decomposed when treated with methyl iodide. *β-Aminodiethyl sulphoxide*, prepared in a similar manner, forms an *oxalate*, m. p. 176°, *picrate*, m. p. 138°, *picrolonate*, decomp. 190°, and, when heated with the calculated quantities of methyl-alcoholic methyl iodide and sodium carbonate, is converted into the *methiodide* of β-dimethylaminodiethyl sulphoxide, m. p. 168°. *Methyl γ-aminopropyl sulphoxide*,

$$CH_3\cdot SO\cdot [CH_2]_3\cdot NH_2,$$

forms an *oxalate*, m. p. 197°, *picrate*, m. p. 143°, and *picrolonate*, decomp. 210°.

Methyl-β-aminoethylsulphone, obtained in the form of the *hydrochloride*, $CH_3\cdot SO_2\cdot CH_2\cdot CH_2\cdot NH_2,HCl$, m. p. 169°, by oxidising the hydrochloride of the sulphide by potassium permanganate, forms a *picrate*, m. p. 167°, *picrolonate*, decomp. 225°, *platinichloride*, decomp. 227°, and *benzoyl* derivative, m. p. 134°, yields the *methiodide* of methyl β-dimethylaminoethylsulphone, m. p. 220°, with methyl-alcoholic methyl iodide at 120°, and is converted into *di-β-methylsulphonethylthiocarbamide*, $SC(NH\cdot CH_2\cdot CH_2\cdot SO_2Me)_2$, m. p. 141°, by carbon disulphide, and into *methyl-β-thiocarbimidoethylsulphone*,

$$SO_2Me\cdot CH_2\cdot CH_2\cdot NCS,$$

m. p. 46—47°, by Hofmann's method with carbon disulphide. *β-Aminodiethylsulphone*, prepared as the *hydrochloride*, m. p. 101—102°, in a similar manner, forms a *picrate*, m. p. 163°, *picrolonate*, decomp. 210°, *platinichloride*, decomp. 227°, *aurichloride*, m. p. 197°, *benzoyl* derivative, m. p. 86°, and *thiocarbamide*, m. p. 141°; the thiocarbimide could not be isolated.

[With WILHELM LOHMANN.]—*Phthalimidodimethyl sulphide*,

$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot CH_2\cdot SMe,$$

m. p. 114°, is obtained from bromomethylphthalimide and sodium methyl mercaptide in alcoholic solution. It is oxidised by hot aqueous potassium permanganate to the *sulphone*, $C_{10}H_9O_4NS$, m. p. 203°. Both the sulphide and the sulphone decompose completely when hydrolysed. C. S.

Chemical Action of Light on Vanillin and its Ethers. ERNESTO PUXEDDU (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 717—723). —When vanillin in solution in alcohol, benzene, or other solvents is exposed to light, dehydrovanillin is obtained in small quantity, and no other product can be detected except a viscous oil. Vanillin methyl and ethyl ethers behave differently when exposed to light in benzene solution, the corresponding methyl and ethyl ethers of vanillic acid being formed respectively. R. V. S.

Reactivity of the Carbonyl Group. HERMANN STAUDINGER (*Annalen*, 1912, **387**, 254—255).—A note explaining more fully the pictorial representation of the unsaturation of an atom by the length of the dotted line representing its residual affinity (compare Staudinger and Kon, Abstr., 1911, i, 876). C. S.

Behaviour of Antimony Trichloride and Tribromide towards certain Oxygenated Organic Compounds. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1785—1804).— The concentration-temperature diagrams given by acetophenone or benzophenone with antimony trichloride or tribromide are all nearly identical, each system being characterised by the formation of one molecular compound, which contains 1 mol. of the ketone to 1 mol. of antimony salt, and melts unchanged. Each diagram consists of four branches, corresponding with (1) the lowering of the m. p. of the ketone by addition of antimony salt, (2) the solubility in the ketone of the molecular compound, (3) the lowering of the m. p. of this compound by the addition of SbX_3, and (4) the lowering of the m. p. of SbX_3 on addition to it of the molecular compound. Each diagram exhibits two eutectic points. The melting points of the various compounds are: $SbCl_3$,COMePh, 60·5°; $SbBr_3$,COMePh, 37·5°; $SbCl_3$,$COPh_2$, 76°; $SbBr_3$,$COPh_2$, 48·5°. The eutectic temperatures and the corresponding numbers of ketone mols. (*n*) per mol. of antimony salt are as follows:

System.	M. p. Ketone.	1st eutectic point. Temperature.	*n*.	2nd eutectic point. Temperature.	*n*.	M. p. SbX_3.
$SbCl_3$—COMePh	19·5°	1°	4·05	32°	0·36	73°
$SbBr_3$—COMePh	19·5	1·5	3·17	31	0·6	94
$SbCl_3$—$COPh_2$	48	35	4·63	39	0·26	73
$SbBr_3$—$COPh_2$	48	29	2·82	40	0·5	94

Benzoic acid (m. p. 120°) forms a molecular compound with neither antimony trichloride nor tribromide, the concentration-temperature diagram consisting, in each case, of two branches meeting at the following eutectic points: $SbCl_3$,0·52Ph·CO_2H, 46°;

$SbBr_3$,0·42Ph·CO_2H, 79°.

The system $SbCl_3$–CH_3·CO_2H gives a molecular compound which forms only with difficulty. The first branch of the curve terminates at the eutectic point −9°, corresponding with the composition $SbCl_3$,3·43CH_3·CO_2H. Then begins the curve of solubility of the molecular compound in acetic acid, but this is observable only on seeding with the molecular compound; unless this is done, branch 1 is prolonged below the eutectic point, and probably meets branch 4 in

another eutectic point. Branch 1 shows no arrest corresponding with the eutectic point $CH_3\cdot CO_2H$–$SbCl_3,CH_3\cdot CO_2H$, as the compound is not formed on cooling the solution. Branch 3 cuts branch 4 (lowering of m. p. of $SbCl_3$ on addition of $CH_3\cdot CO_2H$) at the eutectic point, about 19°, corresponding approximately with $SbCl_3,0\cdot94CH_3\cdot CO_2H$; branch 3 can be followed below this eutectic point, but then represents an unstable condition.

The system $SbBr_3$–$CH_3\cdot CO_2H$ forms no molecular compound, the curve consisting of two branches meeting at the eutectic point 4°, which corresponds with $SbBr_3,4\cdot34CH_3\cdot CO_2H$.

Benzoyl chloride forms no molecular compound with antimony chloride or bromide, each curve showing a single eutectic point: $SbCl_3,1\cdot95Ph\cdot COCl$, −33°, and $SbBr_3,5\cdot45Ph\cdot COCl$, −6°. T. H. P.

The Reduction of Poly-unsaturated Ketones with Crossed Double Linkings by Paal's Method. WALTHER BORSCHE (*Ber.*, 1912, **45**, 46—53).—The author has already successfully applied Paal's reduction method to the preparation of saturated ketones from such unsaturated ketones as cinnamylideneacetone (Abstr., 1911, i, 880), and now extends the investigation to ketones in which each of the two carbon atoms adjacent to the carbonyl group has a double linking. The results indicate that where there is only one double bond on each side of the carbonyl group, the reduction proceeds smoothly, but that in other cases there is considerable formation of resinous substances as by-products.

The reduction of distyryl ketone yields di-β-phenylethyl ketone, b. p. 224°/18 mm.; the oxime melts at 95—96° (compare Dünschmann and von Pechmann, Abstr., 1891, 674); a small quantity of a *substance*, $C_{34}H_{34}O_2$, m. p. 126°, was also obtained. Di-*p*-methoxystyryl ketone is reduced to *αε-di*-p-*methoxyphenylpentan-γ-one*, which crystallises in needles, m. p. 52°.

Di-*o*-hydroxystyryl ketone gives *αε-di*-o-*hydroxyphenylpentan-γ-one*, a viscid mass, which, when heated, loses water with the formation of *tetrahydrodibenzo*spiro*pyran* (compare Decker and Felser, Abstr., 1908, i, 906), which crystallises in needles, m. p. 110°, b. p. 217°/16 mm.

1 : 3-Dibenzylidene*cyclo*pentan-2-one gives 1 : 3-*dibenzyl*cyclo*pentan*-2-*one* as an oil, b. p. 232—233°, which slowly crystallises in needles, m. p. 47°. In a similar manner, 1 : 3-dibenzylidene*cyclo*hexan-2-one and 1 : 3-dibenzylidene*cyclo*heptan-2-one give the corresponding 1 : 3-*dibenzyl*cyclo*hexan-2-one*, m. p. 114°, and 1 : 3-*dibenzyl*cyclo*heptan-2-one*, b. p. 261—262°/28 mm.

Phenyl cinnamylidenemethyl ketone produces *phenyl δ-phenylbutyl ketone*, b. p. 225—226°; the *oxime* forms prismatic crystals, m. p. 81—82°, and by the Beckmann rearrangement changes into the *anilide* of *δ-phenylvaleric acid*, m. p. 89—90°.

Styryl cinnamylidenemethyl ketone gives *αη-diphenylheptan-γ-one*, b. p. 239°/14 mm.; the *semicarbazone* is an oil, whilst the *hydrazone phenylcarbamate*, $CH_2Ph\cdot CH_2\cdot C(N\cdot NH\cdot CO\cdot NHPh)\cdot[CH_2]_3\cdot CH_2Ph$, has m. p. 122—123°.

Dicinnamylideneacetone gives *αι-diphenylnonan-ε-one* (*δ-phenylbutyl ketone*), an oil, b. p. 258—260°/13 mm., which solidifies in a freezing

mixture; the *oxime* and *semicarbazone* are liquids, whilst the *hydrazone phenylcarbamate* forms silky needles, m. p. 129—130°.

2 : 6-Di-cinnamylidene*cyclo*hexanone gives 2 : 6-*di-ω-phenylpropyl*-cyclo*hexanone* as a viscous oil, b. p. 276—278°. D. F. T.

Synthesis of Butin. A. Göschke and Josef Tambor (*Ber.*, 1912, **45**, 186—188. Compare Abstr., 1912, i, 30).—The authors have succeeded in transforming synthetic butein into butin (compare Perkin and Hummel, Trans., 1904, **85**, 1459), thus completing the synthesis of both these natural products. *Butin triacetate* has m. p. 123°.

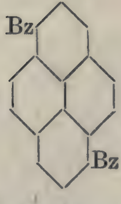
By the action of 3 : 4-dimethoxybenzaldehyde on resacetophenone and resacetophenone dimethyl ether respectively, they have prepared the 3′ : 4′-*dimethyl ether* of *butein* (m. p. 203°) and *butein tetramethyl ether* (m. p. 89°).

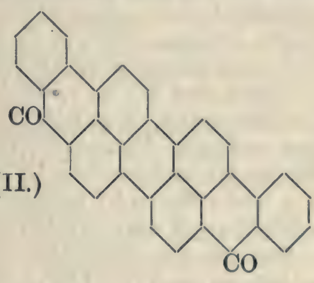
2′ : 4′ : 2-*Trihydroxychalkone*, prepared by condensation of salicylaldehyde with resacetophenone, crystallises in orange needles $+1H_2O$, and has m. p. 185°. Its transformation into 3 : 2′-dihydroxyflavanone appears to be difficult. H. W.

Preparation of Benzanthrone and its Derivatives. Roland Scholl (D.R.-P. 239761).—When aromatic mono- or poly-ketones containing a free peri-position with regard to the carbonyl group are heated at about 140—150° with either aluminium chloride or bromide, or ferric chloride, condensation occurs, yielding benzanthrone or pyranthrone derivatives.

The following compounds have been prepared: Benzanthrone from phenyl α-naphthyl ketone. *Naphthabenzanthrone* from 1 : 1′-dinaphthyl ketone, which can be prepared by the interaction of naphthoic acid with naphthalene in the presence of aluminium chloride.

Dibenzoylpyrene (I), m. p. 155°, and *tribenzoylpyrene*, m. p. 235—237°, are prepared by the action of benzoyl chloride on pyrene in the

(I.) 

(II.) 

presence of aluminium chloride and separated by fractional crystallisation from acetic acid; when the former is heated at 160° with aluminium chloride, it yields pyranthrone (Abstr., 1910, i, 271).

Tri-α-naphthoylpyrene, m. p. 218—219°, prepared from pyrene and α-naphthoyl chloride, furnishes *naphthapyranthrone*.

Dibenzoyl-1 : 1′-*dinaphthyl*, obtained from 1 : 1′-dinaphthyl and benzoyl chloride, furnishes *violanthren* (II), a violet powder, whilst

naphthylanthraquinonyl ketone (from anthraquinone-2-carbonyl chloride and naphthalene) gives *phthaloylbenzanthrone*, and *m*-tolyl-1-naphthyl ketone yields *methylbenzanthrone*, brownish-yellow needles, m. p. 164—165°. F. M. G. M.

Ketones Derived from *iso*Myristicin. EVERARDO SCANDOLA (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 47—54).—The author has prepared the α- and β-keto-derivatives of *iso*myristicin, and has attempted to obtain the dimeric form of *iso*myristicin.

The α-ketone is prepared by heating together for some hours the dibromo-derivative of *iso*myristicin (Thoms, Abstr., 1904, i, 47) and sodium methoxide, removing the excess of methyl alcohol, and distilling the residue with steam. After fractionation in a vacuum of the oil which passes over, the pure *α-keto*-derivative of *iso*myristicin, $C_{11}H_{12}O_4$, is preferably obtained by way of the semicarbazide or oxime. It crystallises in small, silky needles, m. p. 93°. It yields a crystalline *bisulphite* compound, which does not melt below 230°. The *oxime*, $C_{11}H_{13}O_4N$, crystallises in very small prisms, m. p. 124°. The *semicarbazone*, $C_{12}H_{15}O_4N_3$, has m. p. 180°. The ketone does not give an hydroxamic acid with Piloty's acid.

The β-ketone of *iso*myristicin was prepared by Hoering's method (Abstr., 1905, i, 902), When the dibromo-derivative of *iso*myristicin is heated with water and acetone in the presence of calcium carbonate (marble) for two hours, the acetone solution separated, and heated for a further two hours and then distilled, *β-bromo-α-hydroxydihydroiso-myristicin*, $C_{11}H_{13}O_4Br$, is obtained. It is a very dense, yellowish-brown oil, with a pungent odour, and it cannot be crystallised or distilled in a vacuum. On treatment of this substance with alcoholic potassium hydroxide, a glycol, OH·CHR·CHMe·OH, should be produced, from which the oxide, $\mathrm{Ar{\cdot}\underset{\diagdown O \diagup}{CH{\cdot}CHMe}}$, and finally its isomeride, the β-ketone, $Ar\cdot CH_2\cdot COMe$, could be obtained. Actually, the raw product of the reaction does not combine with bisulphite, and it gives analytical figures intermediate between those required by the glycol, $C_{11}H_{14}O_5$, and the oxide, $C_{11}H_{12}O_4$, but when it is distilled in a vacuum, most of it passes over at 230—240°/30 mm.; the distillate readily crystallises, and has m. p. 44—45°. After recrystallisation, it forms long, silky needles, m. p. 54—55°, and gives on analysis numbers corresponding with the formula $C_{11}H_{12}O_4$. This substance gives a bisulphite compound, and is evidently the *β-ketone*. The isomerisation of the oxide is best effected by heating the substance in glacial acetic acid with a few drops of concentrated sulphuric acid, and purifying the product by way of the bisulphite compound. The *semicarbazone*, $C_{12}H_{15}O_4N_3$, has m. p. 143—144°. The *oxime*, $C_{11}H_{13}O_4N$, crystallises in tufts of prisms, m. p. 111—112°. The β-ketone was also prepared by reduction of β-nitro*iso*myristicin and hydrolysis of the oxime produced.

Numerous attempts were made by various methods to polymerise *iso*myristicin. In only one case was any new product obtained. When *iso*myristicin is heated for five to ten minutes in glacial acetic acid solution with a trace of concentrated sulphuric acid, a *substance*

is obtained, which crystallises in small prisms, m. p. 232—233°, and may be the dimeric form of *iso*myristicin. The yield is less than 2%.
R. V. S.

Constitution of Chrysophanic Acid. EUGÈNE LÉGER (*Compt. rend.*, 1912, **154**, 281—283. Compare Robinson and Simonsen, Trans., 1909, **95**, 1085; Oesterle, Abstr., 1911, i, 887).—In order to determine the position of the methyl group in chrysophanic acid, the tetranitro-derivative was oxidised with nitric acid (D 1·5). 2 : 4 : 6-Trinitro-3-hydroxybenzoic acid was isolated from the products, but chrysammic acid could not be detected. It follows that the nitro- and hydroxy-groups in tetranitrochrysophanic acid occupy the same positions as they do in tetranitroaloe-emodin, and therefore that the methyl group in chrysophanic acid can only occupy the position assigned to it by Fischer, Falco, and Gross (Abstr., 1911, i, 309). Chrysophanic acid is therefore 1 : 8-dihydroxy-3-methylanthraquinone. This conclusion is confirmed by fusing the acid with potassium hydroxide, when 5-hydroxy*iso*phthalic acid is formed, together with a much smaller amount of 4-hydroxy*iso*phthalic acid and other substances. W. O. W.

Preparation of Anthraquinone Derivatives Containing Sulphur. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 239762).—When diazotised aminoanthraquinones are treated with thiocarbamides, intermediate compounds are formed, which evolve ammonia on treatment with potassium hydroxide, and furnish the corresponding mercaptan. *Carbamylthiolanthraquinone*, $C_{14}H_7O_2{\cdot}S{\cdot}CO{\cdot}NH_2$, orange, yellow crystals, was prepared from α-aminoanthraquinone and thiocarbamide, whilst with phenylthiocarbamide a similar *compound* was produced. F. M. G. M.

[Preparation of Benzoylaminoanthraquinone Derivatives.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 240079).—The preparation of benzoylaminoanthraquinones and their condensation products has previously been described; it is now found that more valuable colouring matters are produced by employing nitrobenzoyl chlorides, subsequently reducing the nitro-group and combining with another molecule of benzoyl chloride before condensing to form the dye.

Benzoyl-p-*aminobenzoyl*-1-*aminoanthraquinone*, yellow crystals, m. p. 315°, is prepared by benzoylating *p*-aminobenzoyl-1-aminoanthraquinone in nitrobenzene solution; *benzoyl*-p-*aminobenzoyl*-2-*aminoanthraquinone* has similar properties.

The tinctorial properties of the following final condensation *products* are tabulated in the original; *p*-aminobenzoyl-1-aminoanthraquinone with succinic acid, m. p. above 300°, with anthraquinonecarbonyl chloride, m. p. 280°, and with 2-anthraquinonylcarbamyl chloride, m. p. above 300°.

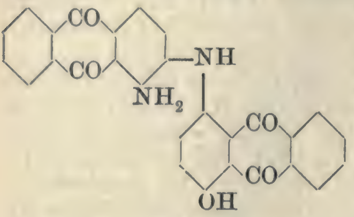
p-Aminobenzoyl-2-aminoanthraquinone with 2-anthraquinonylcarbamyl chloride.

m-Aminobenzoyl-1-aminoanthraquinone with 2-anthraquinonylcarbamyl chloride, m. p. 285°.

3 : 5-Diaminobenzoyl-1-aminoanthraquinone with 2-anthraquinonylcarbamyl chloride (2 mols.), m. p. 235°.

Benzoylaminoanthraquinonecarboxy-1-*aminoanthraquinone* has m. p. above 300°. F. M. G. M.

Preparation of *o*-Aminodianthraquinonylamine Types of Compounds. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 240276).—The *product* (annexed formula), dark blue needles, was



prepared by boiling together 1-amino-4-hydroxyanthraquinone (10 parts), naphthalene (100 parts), anhydrous sodium acetate (5 parts), copper powder (0·2 part), and slowly adding 2-bromo-1-aminoanthraquinone (5 parts); when the latter component is replaced by 2-bromo-1-methylaminoanthraquinone a similar *compound* is obtained, likewise from *a*-amino-4-hydroxyanthraquinone with 1 : 3-dibromo-2-aminoanthraquinone, and from *a*-aminoanthraquinone with 2-bromo-1-aminoanthraquinone. F. M. G. M.

A Supposed Compound of Camphor and Naphthalene. JOUNIAUX (*Bull. Soc. chim.*, 1912, [iv], **11**, 129—132).—When naphthalene containing increasing quantities of camphor is melted and allowed to cool, the temperature at which solidification begins falls steadily from 80° to 32·5°, at which point the mixture contains 58 mols. of camphor to 42 mols. of naphthalene; a similar fall, reaching the same point at the same composition, occurs when increasing quantities of naphthalene are added to camphor. For every mixture, the finishing point of solidification is 32·5°. In view of these facts Girard's supposed compound of these two substances,

$$(C_{10}H_{16}O)_{10},(C_{10}H_8)_7,$$

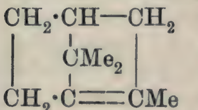
m. p. 32·6° (*J. Pharm. Chim.*, 1891, [v], **24**, 105), appears to have been a eutectic mixture. T. A. H.

Constitution of *iso*Fenchocamphoric Acid and of Some Compounds of the Fenchone Series. OSSIAN ASCHAN [with W. SJÖSTRÖM and A. PETERSON] (*Annalen*, 1912, **387**, 1—85).—The fractions obtained from a very large quantity of pinolene, b. p. below 150° (Abstr., 1907, i, 630), have been separately oxidised by 8% potassium permanganate at 60—80°, whereby carbonic, oxalic, and *dl*-camphoric acids are produced. From these facts and from the molecular refractions of the various fractions, the author deduces that pinolene contains at least three hydrocarbons: (i) *r*-bornylene, b. p. 148—149°, m. p. 40—42°, which yields *dl*-camphoric acid by oxidation; (ii) *a-pinolene*, b. p. 144—146°, a dicyclic terpene, and (iii) *β-pinolene* (cyclo*fenchene*), $C_{10}H_{16}$, a tricyclic terpene, which probably contains a trimethylene ring on account of its stability towards potassium permanganate.

β-Pinolene (*cyclo*fenchene), obtained from the pinolene fractions, b. p. 140—142° and 142—144°, by oxidation as above, has b. p

141·5—143·5°, D_4^{20} 0·8588, $[\alpha]_D$ +0·28°, and n_D^{20} 1·44769 ; its molecular refraction, therefore, exceeds by about 0·6 the value calculated for a tricyclic terpene, a fact which furnishes additional evidence for the presence of a trimethylene ring. By further prolonged oxidation with potassium permanganate, β-pinolene yields a very small quantity of *iso*phthalic acid. This may be due to the presence of a little α-pinolene ; its formation, however, shows that the pinolene hydrocarbons can be converted into benzene derivatives of the meta-series. β-Pinolene in dry ether at −15° forms an unstable, crystalline *hydrochloride*, $C_{10}H_{16}$,HCl, m. p. 27·5—29°.

α-Pinolene hydrochloride, m. p. 38°, has been previously described as pinolene hydrochloride (*loc. cit.*). α-Pinolene probably has the annexed formula ; the halogen atom in its hydrochloride is attached to the CMe group.



β-Pinolene is unchanged by eight hours' boiling with 20% sulphuric acid, but when heated for four hours with 96% alcohol and 96% sulphuric acid yields a dicyclic *ether*, $C_{10}H_{17}$·OEt, b. p. 197—200°, D_4^{20} 0·8904, n_D^{20} 1·45217.

Fractions, b. p. 144·5—146° and 146—148° respectively, of unoxidised pinolene, purified β-pinolene, and also *iso*pinene, have been separately treated at 60—70° with glacial acetic and 50% sulphuric acids by Bertram and Walbaum's method, and the resulting acetates have been hydrolysed. In each case the main product is *dl-iso*fenchyl alcohol (m. p. 43—44°), identified as the phenylurethane, m. p. 95—96°. In the case of the fraction, b. p. 146—148°, a little *iso*borneol is obtained (produced probably from the *r*-bornylene), whilst from the purified β-pinolene a mixture of *dl-iso*fenchyl and *dl*-fenchyl alcohols is formed. By oxidation with potassium permanganate, therefore, the mixture yields *dl-iso*fenchone and *dl*-fenchone, in addition to the chief product, *dl-iso*fenchocamphoric acid (Wallach, Abstr., 1908, i, 809). These facts prove that *dl-iso*fenchyl alcohol is the chief product of the hydratisation of the mixture of fenchenes (consisting mainly of *iso*pinene) obtained from α- and β-pinolenes. A diagrammatic representation of the transformations is given.

A description is given of the preparation in quantity and the purification of *dl-iso*fenchocamphoric acid. It is best obtained from the pinolene fraction, b. p. 140—150°, which is converted into *iso*fenchyl alcohol as above ; the alcohol is then oxidised by alkaline 5% potassium permanganate without warming.

The constitution, $CH_2<\begin{matrix} CH(CO_2H)—CMe_2 \\ CMe(CO_2H)\cdot CH_2 \end{matrix}$, is ascribed to *iso*fenchocamphoric acid on the following grounds. The saturated dibasic acid readily forms an *anhydride*, m. p. 94—95°, by distillation or by treatment with acetyl chloride ; the acid, therefore, has the *cis*-configuration. From the anhydride the *anilic acid*,

$$CO_2H\cdot C_8H_{14}\cdot CO\cdot NHPh,$$

m. p. 191—192°, *ethyl* ester, $C_8H_{14}(CO_2Et)_2$, b. p. 267—268°, D_4^{20} 1·0054, n_D^{21} 1·44626, *methyl hydrogen* ester, m. p. 72—74°, and *ethyl hydrogen* ester, b. p. 289—292° (decomp.), are prepared. The distillation of the

calcium salt, $C_{10}H_{14}O_4Ca$, does not produce a cyclic ketone, indicating that the acid is a substituted succinic or glutaric acid. When heated with acetic and hydrochloric acids at 180° for ten hours, *dl-cis-iso*fenchocamphoric acid is transformed into the less soluble trans-*isomeride*, m. p. 169—170·5°; hence, one of the carboxyl groups is attached directly to a ring carbon atom. When *dl-cis-iso*fenchocamphoric acid is treated with phosphorus pentachloride and the product is brominated as in the case of camphenic acid (Abstr., 1910, i, 709), two stereoisomeric *a-bromo*iso*fenchocamphoric acids*,

$$C_8H_{13}Br(CO_2H)_2,$$

m. p. 208—210° and 160—162° respectively, are obtained. (The author's explanation of the production of the two stereoisomerides is given below.) The former acid, which is the main product, yields an *anhydride*, m. p. 97°, and an *ethyl* ester, b. p. 155—156°/5 mm., D_{15}^{15} 1·2425, and by reduction with zinc and acetic acid regenerates *dl-cis-iso*fenchocamphoric acid. The introduction of only one bromine atom, even when an excess of the halogen is employed, indicates that there is only one hydrogen atom in the α-position to a carboxyl group, whilst the formation of the two stereoisomerides is regarded as evidence that the carbon atom, to which this hydrogen atom is attached, forms part of the alicyclic ring. Other facts in harmony with the preceding constitution of *iso*fenchocamphoric acid are the following. When heated with aqueous sodium carbonate or barium hydroxide, the α-bromo-acid, m. p. 208—210°, yields iso*fencholauronolic acid*, $CO_2H\cdot CMe{<}\begin{matrix}CH{=}CH\\ CH_2\cdot CMe_2\end{matrix}$, m. p. 44—45°, *a-hydroxy*iso*fenchocamphoric acid*, $C_8H_{13}(OH)(CO_2H)_2$, m. p. 185—186° (decomp.), and *dehydro*iso*fenchocamphoric acid*, $C_8H_{12}(CO_2H)_2$, m. p. 189—190°; methods for the separation of these three acids are described. The same three acids are produced by the action of aqueous barium hydroxide on the α-bromo-acid, m. p. 160—162°. When heated above its m. p. or warmed with 50% sulphuric acid, α-hydroxy*iso*fenchocamphoric acid is converted into the lactonic acid, iso*fenchocamphanic acid*, $C_7H_{13}{<}\begin{matrix}CO\text{——}\\ C(CO_2H)\end{matrix}{>}O$, m. p. 177°, which is also produced by heating the α-bromo-acid, m. p. 208—210°, with quinoline at 160° (best method), and is re-converted into α-hydroxy*iso*fenchocamphoric acid by boiling 10% potassium hydroxide.

α-Hydroxy*iso*fenchocamphoric acid is oxidised by lead dioxide and acetic acid to iso*fenchocamphononic acid*,

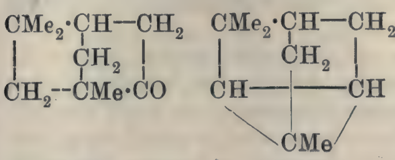
$$CO_2H\cdot CMe{<}\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CMe_2\end{matrix},$$

m. p. 68—70°, which forms a *semicarbazone*, $C_{10}H_{17}O_3N_3$, m. p. 221°. Finally, the fusion of α-hydroxy*iso*fenchocamphoric acid with potassium hydroxide at the lowest possible temperature yields formic acid and an *acid*, $C_9H_{16}O_4$, m. p. 192—193°, which is regarded as identical with Michailenko and Jaworski's $\alpha\alpha\gamma\gamma$-tetramethylglutaric acid, m. p. 185—189°, on account of its stability towards bromine and the formation of an anhydride, m. p. 88°, and p-toluidino-acid,

$$CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot C_7H_7,$$

m. p. 160—161°.

From the preceding constitution of *iso*fenchocamphoric acid, it follows that *iso*fenchone and β-pinolene probably have the constitutions (I) and (II) respectively; the latter can produce fenchyl and *iso*fenchyl alcohols by fission of the trimethylene ring and the addition of water in the two possible ways.



(I.) (II.)

The author assumes the transformation $>CH\cdot CO\cdot \rightarrow >C{:}C(OH)\cdot$ to account for the bromination of aliphatic acids (or, better, their chlorides), the formation of two stereoisomeric α-bromo-acids by the bromination of alicyclic acids, and the transformation, without substitution, of geometric isomerides; thus:

$$(1)\ RR'CH\cdot CO\cdot Cl \rightarrow RR'C{:}CCl\cdot OH \xrightarrow{Br_2} RR'CBr\cdot CClBr\cdot OH \rightarrow RR'CBr\cdot CO\cdot Cl;$$

$$(2)\ {}^{R}_{R'}{>}CH\cdot CO\cdot Cl \rightarrow {}^{R}_{R'}{>}C{:}CCl\cdot OH \rightarrow {}^{R}_{R'}{>}C{<}^{Br}_{CClBr\cdot OH} \text{ and }$$

$$ {}^{R}_{R'}{>}C{<}^{CClBr\cdot OH}_{Br} \rightarrow {}^{R}_{R'}{>}C{<}^{Br}_{CO\cdot Cl} \text{ and } {}^{R}_{R'}{>}C{<}^{CO\cdot Cl}_{Br};$$

$$(3)\ {}^{R}_{R'}{>}C{<}^{H}_{CO_2H} \rightleftarrows {}^{R}_{R'}{>}C{:}C{<}^{OH}_{OH} \rightleftarrows {}^{R}_{R'}{>}C{<}^{CO_2H}_{H}.$$

Although this explanation is equally applicable to transformations of the maleic-fumaric acid type, the author prefers, in such cases, Wislicenus' explanation, because the additive capacity of an ethylenic linking so greatly exceeds that of the carbonyl group in a carboxyl group. C. S.

Constitution of Camphene. KARL AUWERS (*Annalen*, 1912, 387, 240—253).—See this vol., ii, 214.

The Constituents of Ethereal Oils (Derivatives of Natural Cedrene). FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1912, 45, 355—360. Compare Semmler and Hoffmann, Abstr., 1907, i, 946).—Natural cedrene has been oxidised on a larger scale than previously by the action of ozone. The main neutral products are a *ketone*, $C_{14}H_{24}O$ or $C_{14}H_{22}O$, b. p. 120—130°/13 mm. (semicarbazone, m. p. 218°), and the ketonic aldehyde, $C_{15}H_{24}O_2$ (*loc. cit.*); the chief constituent of the acidic portion of the oxidation product is cedreneketonic acid (*loc. cit.*), b. p. 205—215°/10 mm. (methyl ester, b. p. 165—170°/10 mm., D^{20} 1·0509, n_D 1·4882, α_D $-32·4°$ at 20°).

The ketonic acid is probably a methyl-ketonic acid, as it is oxidisable by sodium hypobromite to the dibasic acid, *cedrenedicarboxylic acid*, m. p. 182·5°; the methyl ester (*loc. cit.*) has b. p. 179—183°/13 mm., D^{20} 1·0778, n_D 1·48084, α_D $-31·6°$. D. F. T.

Synthesis of an Aliphatic Terpene. C. J. ENKLAAR (*Chem. Weekblad*, 1912, 9, 68—72. Compare Abstr., 1909, i, 690).—A description of a method for the preparation of labile hydrocarbons of the

olefine series from tertiary alcohols, of the formation of an aliphatic terpene by the dehydration of linalool, and of the behaviour of this product on hydrogenation and ozonisation.

When linalool is brought into contact with active copper at 130—140° in a rapid current of carbon dioxide, the formation of a cyclic hydrocarbon is in large measure obviated, the main product being an aliphatic *hydrocarbon*. The copper was obtained in a very active condition by reducing copper oxide with hydrogen, the oxide being prepared by gentle ignition of copper nitrate. The excess of hydrogen was expelled by carbon dioxide at 170°. The hydrocarbon was separated from the unchanged linalool by repeated vacuum distillation, finally over sodium. It is a liquid, D^{15} 0·804. Acraldehyde, geraniol, and citral were by-products.

The same hydrocarbon was obtained by heating linalool with phenylcarbimide: $2CO:NPh + C_{10}H_{18}O = CO(NHPh)_2 + C_{10}H_{16} + CO_2$. The yield is best with a slight excess of linalool and a temperature of 150—170°, a non-volatile brown oil being obtained as by-product. When the carbimide was in excess, the proportion of this oil was increased by 50%. The hydrocarbon had D^{15} 0·811. The substance was not obtained quite pure, but the following physical constants are given: D^{15} 0·802, n_D^{15} 1·470, b. p. 62°/14 mm., hence it is probably myrcene.

Reduction with nickel and hydrogen at 130° and fractionation of the product yielded a decane, b. p. 159—160°/760 mm. (uncorr.), D^{15} 0·739, identical with $\beta\zeta$-dimethyloctane obtained from ocimene (Abstr., 1908, i, 664). Reduction with sodium and alcohol yielded a hydrocarbon with the odour and b. p. (165—167°) of dihydromyrcene. This substance probably has the formula $C_{10}H_{18}$, because bromination by Baeyer and Villiger's method yielded a crystalline bromide, m. p. 88°, which produced no depression in the m. p. of dihydro-ocimene tetrabromide (compare *Rec. trav. chim.*, 1907, **26**, 167, and **27**, 448).

Ozonisation of the terpene by the method previously described (*ibid.*, 1908, **27**, 422) precipitated an explosive *ozonide*, inflamed by concentrated sulphuric acid, and decomposed by water with formation of acetone, probably succinic acid, and other products not identified.

The impure hydrogenation product yielded an *ozonide* with similar properties. The liquid obtained by the action of water gave the pyrrole reaction distinctly, and probably contained acetone peroxide.

A. J. W.

Reduction of Sabinene. OTTO WALLACH (*Chem. Zentr.*, 1911, ii, 1802; from *Nachr. K. Ges. Wiss. Göttingen*, 1910, 544).—In the presence of metallic catalysts, sabinene takes up 2 atoms of hydrogen with the formation of *dihydrosabinene*, $CH_2<\substack{CH\cdot CHMe \\ | \\ CPr—CH_2}>CH_2$, having b. p. 156—157°, D^{20} 0·8120, n_D^{20} − 2°2′.

W. P. S.

Leaf-Oil of the Washington Cedar (Thuja plicata). ROBERT E. ROSE and CARL LIVINGSTON (*J. Amer. Chem. Soc.*, 1912, **34**, 201—202).—As only a superficial examination of the oil obtained from the leaves of *Thuja plicata* (Brandel, *Pharm. Rev.*, **26**, 248) has hitherto

been made [compare, however, Blasdale, Abstr., 1907, i, 630], a detailed study has now been carried out.

On distillation with steam, the leaves and twigs yielded about 1% of light yellow oil, which had a cedar-like odour, D^{20} 0·913, n_D^{20} 1·4552, $[\alpha]_D^{20}$ −4·77°; acid number, 0·518; ester number, 2·28; saponification number, 2·8, and acetylation number, 8·8. The product was free from phenols, soluble in all proportions in 70% alcohol, and about 85% of it boiled at 100—110°/40 mm. The oil contains tanacetone 80—85%, pinene 3—5%, tanacetyl acetate 1—2%, and tanacetyl alcohol 1—3%.

E. G

The Chemical Degradation of Chitin. HUGO BRACH (*Biochem. Zeitsch.*, 1912, **38**, 468—491).—A description is given of the preparation of the material from *Nephrops norvegicus.* The analyses showed that the substance had a composition corresponding with the formula $C_{32}H_{54}O_{21}N_4$. The estimation of the acetyl groups by a modification of Wenzel's method, which is described by the author, showed that for each nitrogen in the atom there exists an acetyl group. The results indicate that the simplest formula for chitin is one made up of a complex of four acetylglucosamine groups. Lenk's chitosan appears to be formed from chitin by the scission of half the acetyl groups. By the action of nitrous acid, the whole of the nitrogen in the molecule can be eliminated, a fact which the author shows does not contradict the assumption of the presence of acetylamino-groups. S. B. S.

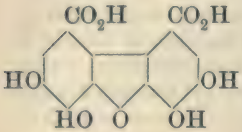
Constitution of Rhein. OTTO A. OESTERLE (*Chem. Zentr.*, 1912, i, 142—143; from *Schweiz. Woch. Chem. Pharm.*, 1911, **49**, 661—665). —Contrary to the view of the author and Riat (Abstr., 1909, i, 946) that aloe-emodin and its most nearly related derivatives are derived from 1:8-dihydroxyanthraquinone (chrysazin), Robinson and Simonsen (Trans., 1909, **95** 1085) regard 1:6-dihydroxyanthraquinone (*iso*chrysazin) as the parent substance of rhein. The author, therefore, has converted rhein through *rhein chloride*, yellow needles, and the *amide*, dark red needles, into an *aminodihydroxyanthraquinone*, $C_{14}H_9O_4N$, m. p. 255° or 258°, red needles, from which, by elimination of the amino-group, impure 1:8-*dihydroxyanthraquinone*, m. p. 182—183° instead of 191—192° (acetate, m. p. 232°), has been obtained. C. S.

Phylloxanthin. LEON MARCHLEWSKI (*Ber.*, 1912, **45**, 24—25).— The phylloxanthin described by Schunck (Abstr., 1885, 1241) is shown to be identical with *allo*chlorophyllan (Marchlewski and Marszałek, Abstr., 1911, i, 735). Phylloxanthin yields 30·02% of phytol instead of 31·8%. On prolonged exposure to concentrated hydrochloric acid, phylloxanthin is converted into basic products, including a substance soluble in 20% hydrochloric acid.

A more recent preparation of phylloxanthin gave a solid substance instead of phytol on hydrolysis. E. F. A.

Tannin. VIII. MAXIMILIAN NIERENSTEIN (*Annalen*, 1912, **386**, 318—332. Compare Abstr., 1910, i, 265).—Purpurotannin, the

amorphous, red oxidation product of penta-acetyl-leucotannin (Abstr., 1909, i, 402), has the composition $C_{14}H_8O_9$, forms a *quinoline* salt, $C_{14}H_8O_9,2C_9NH_7$, dark red needles, and dissolves unchanged in boiling $2N$-potassium hydroxide. It forms a *tetra-acetate*, m. p. 324—327° (decomp.), *tetrabenzoate*, m. p. 279—281° (decomp.), and *tetramethyl ether*, $C_{14}H_4O_5(OMe)_4,H_2O$, m. p. 242—244° (decomp.), and yields diphenylene, not naphthalene, as stated (*loc. cit.*), by distillation with zinc dust. It is shown to be 1 : 2 : 7 : 8 - *tetrahydroxydiphenyleneoxide* - 4 : 5 - *dicarboxylic acid* (annexed formula).



When heated with piperidine (but not with quinoline) at 180°, it yields 1 : 2 : 7 : 8-*tetrahydroxydiphenylene oxide*, $C_{12}H_8O_5$, red needles, m. p. 334—338° (decomp.) (*tetra-acetate*, m. p. 247—251°), whilst by reduction with hydriodic acid and phosphorus at 180° it is converted into diphenylene oxide.

A course of formation of purpurotannin from leucotannin is suggested. The cause of its colour will be discussed later; apparently it is connected with the presence of hydroxyl groups in the peri-position to the oxygen of the furan ring. C. S.

"Luteo-acid" (A Correction). MAXIMILIAN NIERENSTEIN (*Ber.*, 1912, **45**, 365).—The analytical results for the composition of "luteo-acid" (pentahydroxydiphenylmethylolidecarboxylic acid) (Abstr., 1908, i, 897; 1909, i, 174; 1910, i, 265, 389) were low in the percentage of carbon; as the more carefully dried substance gives results agreeing well with the formula $C_{14}H_8O_9$, it is probable that the earlier discrepancies were due to occluded solvent. D. F. T.

Decomposition of Alkylidenehydrazines. Conversion of Furfuraldehyde into 2-Methylfuran. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1563—1565).—When heated in presence of a small quantity of potassium hydroxide, furfurylidenehydrazine decomposes, giving nitrogen and 2-methylfuran, a colourless liquid, b. p. 64°/757 mm., D_0^{20} 0·9159, n_D 1·4344. The constants given for this compound by Atterberg (Abstr., 1880, 663) and by Harries (Abstr., 1898, i, 232) are inaccurate, doubtless on account of impure products being examined. T. H. P.

Coumarandione, the Oxygen Analogue of Isatin. KARL FRIES and W. PFAFFENDORF (*Ber.*, 1912, **45**, 154—162. Compare Abstr., 1910, i, 186; also Stoermer, *ibid.*, 1909, i, 174, and following abstract).—Coumaran-1 : 2-dione, $C_6H_4<\substack{O\\CO}>CO$, is readily prepared by heating a solution of *o*-hydroxyphenylglyoxylic acid in light petroleum with phosphoric oxide, or by distilling the acid under diminished pressure. It crystallises in large, yellow, prismatic plates, m. p. 134°, b. p. 142°/17 mm., and dissolves in concentrated sulphuric acid, yielding a yellowish-red solution, which gradually becomes colourless owing to the loss of carbon monoxide and conversion of the diketone into salicylic acid.

With *o*-phenylenediamine it yields 2-hydroxy-3-hydroxyphenylquinoxaline (Marchlewski and Sosnowski, Abstr., 1901, i, 415). On exposure to air it takes up water with the formation of *o*-hydroxyphenylglyoxylic acid or its hydrate, m. p. 43°.

When heated at 220° under ordinary pressure, it loses carbon monoxide, yielding a ruby-red glassy mass, which sinters at 150°, forms a transparent, viscid liquid at 200°, and finally becomes mobile at 240°. The latter substance is hydrolysed by alkalis in alcoholic solution to salicylic acid, and gives a colloidal solution in chloroform. It probably consists of a polymeric *salicylide*, which, however, is different from the polymerides described previously.

Ethyl o-*hydroxyphenylglyoxylate*, $C_{10}H_{10}O_4$, prepared by boiling coumarandione in alcoholic solution, is a yellow oily liquid, which solidifies in a freezing mixture, m. p. 15°. It readily loses alcohol yielding the original ketone.

Coumaran-1:2-dione-2-phenylhydrazone, $O<\begin{matrix}C_6H_4\\CO\end{matrix}>C:N\cdot NHPh$, obtained from its components in glacial acetic acid solution, crystallises in lustrous, yellow plates, m. p. 185°, and is hydrolysed by alkalis in alcoholic solution to the *phenylhydrazone* of *o*-hydroxyphenylglyoxylic acid, $C_{14}H_{12}O_3N_2$. This crystallises in light yellow needles, m. p. 148° (decomp.), and is also obtained by heating *o*-hydroxyphenylglyoxylic acid with phenylhydrazine in aqueous solution. It readily loses water, yielding coumarandione-2-phenylhydrazone.

The *anil* of *o*-hydroxyphenylglyoxylic acid, $C_{14}H_{11}O_3N$, prepared by heating coumarandione with aniline in benzene or alcoholic solution, crystallises in pale yellow plates, m. p. 102°, and shows no tendency to form a lactone; the *acetyl* derivative has m. p. 138°.

The p-*dimethylaminoanil*, $OH\cdot C_6H_4\cdot C(:N\cdot C_6H_4\cdot NMe_2)\cdot CO_2H$, crystallises in dark red needles of a metallic lustre, m. p. 153°; the *monosodium* salt and *monohydrochloride*, crystallising in yellow prisms, are mentioned. On treatment with phenylhydrazine, the *p*-dimethylaniline residue is eliminated with the formation of the phenylhydrazone of *o*-hydroxyphenylglyoxylic acid. With *o*-phenylenediamine it yields 2-hydroxy-3-hydroxyphenylquinoxaline.

When hydrolysed with aqueous alcoholic sodium hydroxide and the resulting solution neutralised with acetic acid, coumaran-1:2-dione-1-*p*-dimethylaminoanil (Fries and Hasselbach, Abstr., 1911, i, 151) is converted into o-*hydroxyphenylglyoxylo*-p-*dimethylaminoanilide*, $OH\cdot C_6H_4\cdot CO\cdot CO\cdot NH\cdot C_6H_4\cdot NMe_2$, which, however, could not be obtained in a pure condition, and was, therefore, characterised by means of its *benzoyl* derivative, $C_{23}H_{20}O_4N_2$, stout, red prisms, m. p. 138°.

With excess of bromine in glacial acetic acid solution, coumarandione yields 3:5-dibromo-2-hydroxyphenylglyoxylic acid, which has m. p. 148° (decomp.) (compare Abstr., 1910, i, 332), and forms a *hydrate*, $C_8H_4O_4Br_2,H_2O$, crystallising in slender, pale yellow needles, m. p. 110°.

1-*Bromo-2-coumaranone*, $C_8H_5O_2Br$, prismatic needles, m. p. 87°, and 1:1-*dibromo-2-coumaranone*, $C_8H_4O_2Br_2$, pale yellow needles, m. p. 142°, are obtained by brominating 2-coumaranone in carbon tetra-

chloride solution. When warmed with sulphuric acid, the dibromo-compound is converted into coumarandione, and finally into salicylic acid. On treatment with *o*-phenylenediamine it yields coumarophenazine. 1 : 1-*Dichloro-2-coumaranone*, prepared by chlorinating 2-coumaranone in glacial acetic acid solution, forms white, prismatic needles, m. p. 70°. F. B.

Coumarandione, the Analogue of Isatin in the Coumarone Series. A Correction. RICHARD STOERMER (*Ber.*, 1912, 45, 162—163. Compare preceding abstract).—The compound described previously (Abstr., 1909, i, 174) as the hydrate of coumarandione is now found to be the *acetyl* derivative of 1-oximino-2-coumaranone,

$$C_6H_4<\substack{CO\\ -O-}>C{:}N\cdot OAc.$$

It is shown that the substance is formed by the action of acetic acid on *aci*-nitrocoumaranone, and not by the oxidation of "*leuco*-oxindigo," as previously supposed.

With respect to the mechanism of the reaction, the author imagines that an intermediate compound of the composition

$$C_6H_4<\substack{CO\\ -O-}>CH\cdot NO(OH)\cdot OAc$$

is first produced by the combination of acetic acid and *aci*-nitrocoumaranone, and that this is subsequently reduced by the nitrous acid formed by the spantaneous decomposition of the *aci*-nitro-compound, loss of 1 mol. of water taking place simultaneously.

F. B.

Constitution of the Desaurins. C. KELBER and A. SCHWARZ (*Ber.*, 1912, 45, 137—147).—By the interaction of carbon disulphide, potassium hydroxide, and ketones of the type $R\cdot CO\cdot CH_2\cdot R$, Meyer (Abstr., 1888, 484; 1890, 1144; 1892, 340, 1127) obtained a number of desaurins, to which he ascribed the constitution:

$$R\cdot CO\cdot CR{:}C<\substack{S\\ S}>C{:}CR\cdot CO\cdot R\ (R = \text{aryl}).$$

This formula has now been confirmed by the synthesis of similarly constituted desaurins (II) by the removal of hydrogen sulphide from 2 mols. of the aryl $\beta\beta$-dithiolvinyl ketones of the formula I:

$$\text{(I) } R\cdot CO\cdot CH{:}C(SH)_2 = \text{(II) } R\cdot CO\cdot CH{:}C<\substack{S\\ S}>C{:}CH\cdot COR + H_2S.$$

A number of desaurins of the type $R\cdot CO\cdot CMe{:}C<\substack{S\\ S}>C{:}CMe\cdot COR$ have also been prepared by heating aryl ethyl ketones, R·COEt, with carbon disulphide and finely-powdered potassium hydroxide.

The *compound*, $COPh\cdot CH{:}C{:}S_2{:}C{:}CH\cdot COPh$, is obtained in small yield by heating phenyl $\beta\beta$-dithiolvinyl ketone (Kelber, Abstr., 1910, i, 390) at 100°. It is also produced together with carbon oxysulphide, benzophenone, and benzoyl sulphide by rapidly heating the dibenzoyl derivative of the ketone (*loc. cit.*) either alone at 210°, or in solvents of high b. p., such as ethyl benzoate or acetophenone. It crystallises from ethylene dibromide in yellow, rectangular prisms, m. p. 212—214° (decomp.), and dissolves in strong sulphuric acid, yielding orange-red solutions having an intense green fluorescence.

The *lead* salt of phenyl $\beta\beta$-dithiolvinyl ketone, $C_9H_6OS_2Pb$, is a heavy, reddish-brown powder; the *mercuric* salt, $C_{18}H_{14}O_2S_4Hg$, is soluble in organic solvents, and crystallises from toluene in orange needles, which have m. p. 185—190° (decomp.), with previous darkening at 130—140°. When heated in solvents of high b. p., both the lead and mercuric salts are decomposed with the formation of metallic sulphide and the above-mentioned desaurin.

The *monothiourethane*, $COPh\cdot C_2H_2S_2\cdot CO\cdot NHPh$, obtained from phenyl $\beta\beta$-dithiolvinyl ketone and phenylthiocarbimide in benzene solution, crystallises in slender needles, m. p. 94° (decomp.), and when carefully heated gives a small yield of the corresponding desaurin.

The *compound*, $(C_4H_3S\cdot CO\cdot CH\dot{:}C)_2S_2$, may be prepared from α-thienyl $\beta\beta$-dithiolvinyl ketone (Abstr., 1911, i, 740) by methods similar to those employed in the case of the preceding desaurin. It crystallises in moss-like aggregates of slender, yellow needles, which decompose at 260° with previous darkening, and yields with sulphuric acid deep red solutions having a green fluorescence.

The *mercuric* salt of α-thienyl $\beta\beta$-dithiolvinyl ketone, $C_7H_4OS_3Hg$, is obtained from mercuric chloride and the ketone in alcoholic solution.

The *thiourethane*, $C_4H_3S\cdot CO\cdot C_2H_2S_2\cdot CO\cdot NHPh$, prepared from the ketone and phenylthiocarbimide, decomposes at 80°.

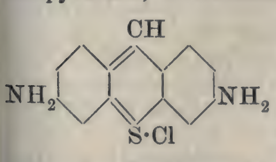
The *desaurin* from p-tolyl $\beta\beta$-dithiolvinyl ketone (*loc. cit.*) crystallises in yellow, rectangular prisms.

The *compound*, $COPh\cdot CMe\dot{:}C\dot{:}S_2\dot{:}C\dot{:}CMe\cdot COPh$, prepared by heating phenyl ethyl ketone with carbon disulphide and potassium hydroxide, crystallises in lustrous, golden-yellow leaflets, m. p. 225°; the *compound*, $(C_6H_4Me\cdot CO\cdot CMe\dot{:}C)_2S_2$, from p-(?)tolyl ethyl ketone in strongly refractive, yellow needles, m. p. 263—265°. The *compound*,

$$(C_4H_3S\cdot CO\cdot CMe\dot{:}C)_2S_2,$$

from α-thienyl ethyl ketone forms yellow needles, m. p. 258—260°; the *compound*, $(C_{10}H_7\cdot CO\cdot CMe\dot{:}C)_2S_2$, from β-naphthyl ethyl ketone crystallises in yellow leaflets, which have m. p. 264°, and decompose at 268—269°. F. B.

The Simplest Thiopyronine. FRIEDRICH KEHRMANN and L. LÖWY (*Ber.*, 1912, 45, 290—292).—The chloride of the simplest thiopyronine, 3 : 6-*diaminothioxanthinium chloride* (annexed formula) is

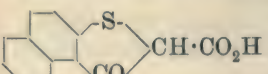


obtained in small yield by the addition of a glacial acetic acid solution of di-p-acetylaminodiphenylmethane to a solution of flowers of sulphur in fuming sulphuric acid at a temperature not exceeding 10°, and subsequent hydrolysis of the resulting 3 : 6-*diacetylaminothioxanthinium sulphate* (not isolated). It crystallises from alcohol in metallic green needles or prisms, which yield scarlet-red solutions having a greenish-yellow fluorescence. The *carbonate*, *acetate*, *iodide*, *dichromate*, and also the *nitrate*, crystallising in scarlet-red needles, are described; the *platinichloride*, $(C_{13}H_{11}N_2SCl)_2PtCl_4$, was analysed.

Elimination of one of the amino-groups from the preceding chloride

by successive treatment with nitrous acid (1 mol.) and alcohol results in the formation of apo*thiopyronine* (3-*aminothioxanthinium*) *chloride*, $NH_2 \cdot C_6H_3 < \frac{CH}{SCl} > C_6H_4$, which was converted into a red, crystalline *nitrate* and *platinichloride*, $(C_{13}H_{10}NSCl)_2PtCl_4$. F. B.

[Preparation of Ketonaphthathiophen.] KALLE & Co. (D.R.-P. 239093).—Derivatives of *o*-carboxynaphthylthiolacetic acids yield valuable dyes, and the following series of compounds have been prepared: α-Naphthylamine-2-sulphonic acid is converted by diazotisation and subsequent treatment with copper sulphate and potassium cyanide into *sodium* 1-*cyanonaphthalene*-2-*sulphonate*, leaflets, which furnishes an acid *chloride*, long needles or prisms, m. p. 143°; this when reduced with zinc dust in sulphuric acid solution and treated with chloroacetic acid yields a mixture of 1-*cyanonaphthalene*-2-*thiolacetic acid* and 1-*carboxynaphthalene*-2-*thiolacetic acid*, which can be separated by fractional crystallisation from water, when the acid is obtained in long, colourless needles, m. p. 93° and (when anhydrous) 127—128°.



Ketonaphth thiophencarboxylic acid (annexed formula), colourless aggregates, is obtained by the fusion of the foregoing mixture with sodium hydroxide, and is converted by treatment with mineral acids into *naphthoxythiophen*, glistening, grey crystals, m. p. 118—119°. F. M. G. M.

[Preparation of Indigoid Compounds.] KALLE & Co. (D.R.-P. 239916).—When indoxyl, oxythionaphthens, or compounds of the same type (2 mols.) are condensed with a dialdehyde or diketone (1 mol.), substances are obtained having the general formula:

$$C_6H_4 < \frac{CO}{X} > C:CR' \cdot R \cdot CR'':C < \frac{CO}{Y} > C_6H_4,$$

where R is a hydrocarbon; R′, R″ hydrogen or hydrocarbon residues; X and Y alike or different atoms or groups, such as sulphur, oxygen or the imino-group.

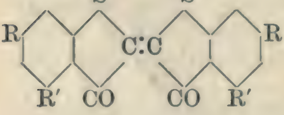
The yellow, crystalline compound,

$$C_6H_4 < \frac{CO}{S} > C:CH \cdot C_6H_4 \cdot CH:C < \frac{CO}{S} > C_6H_4,$$

was prepared from ketothionaphthen (2 mols.) and terephthalaldehyde (1 mol.), whilst the analogous compound obtained from the bisulphite derivative of glyoxal (1 mol.) forms brownish-yellow needles. The ketothionaphthens can be replaced by indoxyls in these reactions.

F. M. G. M.

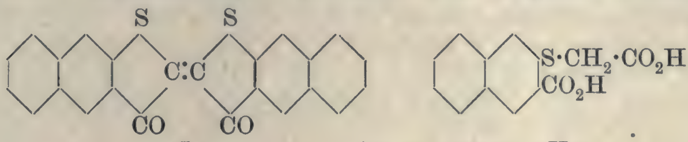
[Preparation of "Dihalogendimethylthioindigos."] KALLE & Co. (D.R.-P. 239094).—The symmetrical "dihalogendimethylthioindigos" of the annexed general formula (where R is a halogen atom and R′ a methyl group, or vice versa) are of technical value, and in this connexion the following compounds have been prepared.



5-*Chloro*-3-*amino*-o-*toluic acid*, needles (prepared by the reduction of the corresponding chloronitrotoluic acid), when diazotised, xanthogenated, and treated with chloroacetic acid, yields 5-*chlorophenyl*-3-*methyl*-2-*carboxyphenylthiolacetic acid*, colourless needles, which on fusion with sodium hydroxide furnishes 6-*chloro*-3-*hydroxy*-4-*methyl*-(1)-*thionaphthen*-o-*carboxylic acid*, and subsequently on treatment with mineral acid, 6-*chloro*-3-*hydroxy*-4-*methyl*-(1)-*thionaphthen*, glistening, colourless needles.

The reaction is stated to be applicable to other halogenated nitrotoluic acids. F. M. G. M.

[Preparation of "Naphthioindigo."] KALLE & Co. (D.R.-P. 240118).—"*Naphthioindigo*" (formula I) is prepared as follows:



(I.) (II.)

2-amino-3-naphthoic acid is diazotised and converted successively into 2-*thionaphthol*-3-*carboxylic acid*, a yellow powder, m. p. 275—276°, and 3-*carboxynaphthyl*-2-*thiolacetic acid* (II), a colourless, crystalline powder, m. p. 203°; this when treated with alkali or acetic anhydride yields 3-*keto*-(1)-*thioanthren*, and by subsequent oxidation with potassium ferricyanide the foregoing "naphthioindigo." F. M. G. M.

Bromo-derivatives of the Alkaloids of Peganum harmala and their Basic Derivatives. V. HASENFRATZ (*Compt. rend*, 1912, **154**, 215—217. Compare Fischer, Abstr., 1889, 730; 1898, i, 160). —On treating harmaline, harmine, *apo*harmine, and methyl*apo*harmine with bromine in acetic acid, the *hydrobromides* of the corresponding monobromo-derivatives are obtained. *Bromoharmaline*, $C_{13}H_{13}ON_2Br$, crystallises in colourless, slender needles, m. p. 195°; the *hydrochloride* and *platinichloride* are yellow. In the case of harmine, two isomeric compounds are formed, and may be separated by heating the hydrobromides at 50°, *bromoharmine hydrobromide* alone fusing at this temperature. *Bromoharmine*, $C_{13}H_{11}ON_2Br$, occurs in orthorhombic prisms, m. p. 275°; the salts crystallise from alcohol, but form jellies with water. *iso*Bromoharmine crystallises in long needles, m. p. 203°, and its salts crystallise from water; the *platinichloride* is orange-red. *Bromo*apo*harmine*, $C_8H_7N_2Br$, crystallises in long needles, m. p. 229°, and *bromomethyl*apo*harmine*, $C_9H_9N_2Br$, in needles, m. p. 196°.

On brominating harmine in presence of sulphuric acid, and suspending the product, Fischer's supposed tetrabromide, in hot dilute alcohol, slender needles of *dibromoharmine monohydrobromide* are obtained; when treated with ammonia this gives *dibromoharmine*, $C_{13}H_{10}ON_2Br_2$, m. p. 209°. Fischer's compound appears to be the *dihydrobromide* of this base. W. O. W.

Preparation of a Compound of Codeine with Diethylbarbituric Acid. KNOLL & Co. (D.R.-P. 239313).—*Codeine*

diethylbarbiturate, prisms, m. p. 85°, is readily prepared by mixing molecular proportions of codeine and diethylbarbituric acid (veronal) in aqueous or alcoholic solution, or by intimately mixing codeine hydrochloride with sodium diethylbarbiturate in the absence of solvents. F. M. G. M.

Degradation of Sparteine. Formation of a Hydrocarbon: Sparteilene. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1912, **154**, 161—163. Compare Abstr., 1908, i, 43, 44, 563).—When methylhemisparteine is treated with methyl iodide, the product has the composition, $C_{15}H_{22}N_2Me_2I$, but appears to consist of a mixture of at least two isomerides. On treatment with silver oxide, it gives a quaternary ammonium base, which, on heating in a vacuum, yields inactive *dimethylhemisparteilene*, $C_{15}H_{21}NMe_2$, b. p. 201—202°/27·5 mm. This substance forms a *methiodide* and a quaternary *hydroxide*; the latter decomposes at 75° in a vacuum, giving trimethylamine and *sparteilene*, $C_{15}H_{20}$. The new hydrocarbon is a colourless, odourless, optically inactive liquid, b. p. 157—159°/18 mm., showing a molecular refraction corresponding with the existence of six ethylenic linkings. Its production with trimethylamine, taken in conjunction with the formation of methylsparteilene and trimethylamine from dimethylsparteine, is sufficient to establish the symmetrical character of the sparteine molecule. Oxidation of sparteilene by means of potassium permanganate leads to the formation of an *acid*, $C_{10}H_{10}O_5$, m. p. 300—305° on the Maquenne block. W. O. W.

Strychnos Alkaloids. XIV. Derivatives and Decomposition Products of Brucinolone. Decomposition of Dihydrobrucinonic Acid into *iso*Brucinolone and Glycollic Acid. HERMANN LEUCHS and J. F. BREWSTER (*Ber.*, 1912, **45**, 201—221. Compare Abstr., 1908, **i**, 563; 1909, **i**, 253, 954).—For the preparation of brucinolone, brucine, dissolved in acetone, was oxidised by potassium permanganate, whereby brucinonic and dihydrobrucinonic acids were obtained. The two acids are difficult to separate completely. Brucinolic acid was obtained by reduction of brucinonic acid (containing some dihydrobrucinonic acid). This latter acid appears to be formed even when the most carefully purified keto-acid is reduced, and the authors have come to the conclusion that it is stereoisomeric with brucinolic acid, since they were also able to show that the two acids are similarly affected by sodium hydroxide. Since dihydrobrucinonic acid is formed by the direct oxidation of brucine, it follows that the latter must contain a secondary alcoholic group.

For the conversion of brucinolic acid into brucinolone, the authors recommend the use of normal sodium hydroxide ($1\frac{1}{4}$ mols. instead of $1\frac{1}{2}$ mols. previously employed). The m. p. of brucinolone is now given as about 270°, and $[\alpha]_D^{22}$ $-34·7°$. The latter value is somewhat dependent on concentration and source of light used.

By means of ice-cold nitric acid (D 1·4), brucinolone was converted into *nitrobis*apo*methyldehydrobrucinolone*, which forms orange-coloured leaflets.

Bis*apo*methylbrucinolone (bisdemethylbrucinolone of Abstr., 1909,

i, 954) was converted into the *triacetate* by treatment with acetic anhydride and sodium acetate. It crystallises in colourless leaflets, m. p. 260—261°.

In brucinolone hydrate I. (in which the $\vdots$N–CO– of brucinolone is supposed to have been transformed into $\vdots$NH HO_2C–), the presence of the imino-group has been proved by the regeneration of brucinolone by the action of heat on the hydrate I., and by the formation of a *derivative* when treated with phenylcarbimide. The latter is a non-crystallisable, amorphous, white powder, m. p. 192° (decomp.) after previous softening. The presence of the carboxyl group is shown by the isolation of the *hydrochlorides* of the methyl ester, m. p. 189—190° (decomp.), and of the ethyl ester, m. p. 181° (decomp.).

The isolation of a by-product, $C_{21}H_{24}O_6N_2$, during the action of sodium hydroxide on brucinolic acid has been previously described (Abstr., 1909, i, 954). This substance when heated with 5*N*-hydrochloric acid yields a *hydrochloride*, which is completely melted at 255° after previous gas evolution. The free *base* obtained from this, which has been named brucinolone hydrate II., separates from water with varying amounts of water of crystallisation. It has m. p. 240° (decomp.), after softening at 190°. It differs from the hydrate I. in possessing less tendency to lose water. When the by-product, $C_{21}H_{24}O_6N_2$, is heated with sodium hydroxide, brucinolone is formed.

In order to gain further insight into the oxidation products of brucine, *brucinolone acetate* (m. p. 253—254°) was prepared by heating brucinolone with acetic anhydride and sodium acetate. This was oxidised in acetone solution by potassium permanganate. In this manner an *acid*, $C_{23}H_{24}O_9N_2$, was isolated, which gave a brownish-red coloration with alcoholic ferric chloride, and thus appears to be a keto-acid. When heated, it softens at 120°, melts at about 160° (decomp.), then solidifies, becoming yellow at 240°, and melting again at about 275°. When heated during ten minutes at 160—180°, it evolves carbon dioxide and leaves a neutral *substance*, $C_{20}H_{24}O_7N_2$, which has m. p. about 281°. During the oxidation, a neutral *product*, $C_{23}H_{22}O_6N_2$ (m. p. about 312°), is also formed.

By the action of normal sodium hydroxide ($1\frac{1}{2}$ mols.) on dihydrobrucinonic acid, glycollic acid was obtained together with iso*brucinolone*. The latter forms yellow crystals, m. p. 308° (decomp.), and has $[\alpha]_D^{24}$ +26·9° in glacial acetic acid solution. H. W.

Action of Acetic Anhydride on Some Benzylideneanthranilic Acids. JOHN B. EKELEY and PAUL M. DEAN (*J. Amer. Chem. Soc.*, 1912, **34**, 161—164).—The products of the condensation of anthranilic acid with aromatic aldehydes (compare Wolf, Abstr., 1911, i, 735) react with acetic anhydride to form a series of oxazines which are crystalline, very stable, and usually colourless.

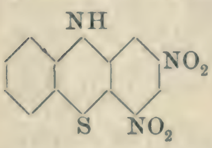
Benzylideneanthranilic acid, m. p. 126°, yields 1-*keto*-4-*acetyl*-3-*phenyl-dihydro*-2 : 4-*benzoxazine*, $C_6H_4<\begin{matrix}CO—O\\ NAc·CHPh\end{matrix}$, m. p. 108°, which when heated with hydrochloric acid is decomposed into benzaldehyde and acetylanthranilic acid. *m*-Nitrobenzylideneanthranilic acid, m. p. 202°, and *p*-nitrobenzylideneanthranilic acid, m. p. 164°, yield 1-*keto*-

4-*acetyl*-3-m- and -p-*nitrophenyldihydro*-2 : 4-*benzoxazines*, m. p. 192° and 199° respectively. When *p*-hydroxybenzylideneanthranilic acid, m. p. 207°, is heated with acetic anhydride, 1-*keto*-4-*acetyl*-3-p-*acetoxyphenyldihydro*-2 : 4-*benzoxazine*, m. p. 148°, is produced. Salicylideneanthranilic acid, m. p. 195°, similarly gives 1-*keto*-4-*acetyl*-3-o-*acetoxyphenyldihydro*-2 : 4-*benzoxazine*, m. p. 162°. *Vanillylideneanthranilic acid*, m. p. 170°, crystallises in lemon-yellow needles, and when heated with acetic anhydride yields 1-*keto*-4-*acetyl*-3-p-*hydroxy*-m-*methoxyphenyldihydro*-2 : 4-*benzoxazine*, m. p. 184°, which forms pale straw-coloured needles. E. G.

Thiazines. RICHARD MÖHLAU, HEINRICH BEYSCHLAG, and H. KÖHRES (*Ber.*, 1912, **45**, 131—137. Compare Abstr., 1910, i, 337).—The authors have repeated the work of Kehrmann and Steinberg (Abstr., 1911, i, 1034), and agree with them that the dinitrophenthiazine, obtained by the interaction of picryl chloride and *o*-aminothiophenol, has the constitution originally ascribed to it by Kehrmann and Schild (Abstr., 1900, i, 61). The synthesis of the isomeric 2 : 4-dinitrophenthiazine is also described.

Di-*o*-aminodiphenyl disulphide is best prepared by reducing di-*o*-nitrodiphenyl disulphide (Blanksma, Abstr., 1901, i, 460) with hydrazine hydrate in alcoholic solution.

The *dibenzoyl* derivative, $(NHBz\cdot C_6H_4)_2S_2$, crystallises in pale yellow needles, m. p. 141°, and is reduced by aqueous sodium sulphide to o-*benzoylaminophenyl mercaptan*, which reacts with picryl chloride in the presence of sodium acetate, yielding *trinitrophenyl* o-*benzoylaminophenyl sulphide*, $NHBz\cdot C_6H_4\cdot S\cdot C_6H_2(NO_2)_3$. The latter compound crystallises in yellow prisms, m. p. 169°, and when boiled with sodium hydroxide in aqueous alcoholic solution is converted into 2 : 4-*dinitrophenthiazine* (annexed formula), which crystallises in almost black, lustrous prisms, m. p. 218° (appearing reddish-brown by transmitted light), dissolves in alcoholic sodium hydroxide, yielding bluish-violet solutions, and on reduction with stannous chloride and hydrochloric acid is converted into 2 : 4-*diaminophenthiazine stannichloride*,



$$4C_6H_4<^{NH}_{S}>C_6H_2(NH_2,HCl)_2,SnCl_4.$$

This forms brownish-yellow needles, and is oxidised by ferric chloride in alcoholic solution in the presence of hydrochloric acid to 2 : 4-*diaminophenazthionium chloride*, $C_6H_4<^{N}_{SCl}>C_6H_2(NH_2)_2$. The *ferrichloride*, $C_{12}H_{10}N_3SCl_4Fe,H_2O$, forms greenish-black, microscopic crystals, which lose their water of crystallisation at 110°; the *platinichloride*, *chromate*, *carbonate*, and the thiazonium *base* itself are briefly mentioned.

Kehrmann and Steinberg's 1 : 3-dinitrophenthiazine has m. p. 187°. F. B.

Decomposition of Alkylidenehydrazines. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1554—1562).—The author has

been able to pass from carone through carylidenehydrazine to carane (compare Abstr., 1911, i, 1028), the hydrocarbon thus obtained being structurally identical with that prepared from pulegone, but exhibiting a lævo- instead of a dextro-rotation.

Carylidenehydrazine, $CMe_2<\begin{matrix}CH\cdot C(:N\cdot NH_2)\cdot CHMe \\ CH\text{——}CH_2\text{——}CH_2\end{matrix}$, obtained by the action of hydrazine hydrate on carone, is a viscous liquid, b. p. 131°/20 mm., D_0^{20} 0·9683, n_D 1·5082, $[\alpha]_D$ +375·7—378·8° (absolute alcohol). Its *thioureide*, $NHPh\cdot CS\cdot NH\cdot N:C_{10}H_{16}$, forms hexagonal plates, m. p. 100—101°. Hydrolysis of carylidenehydrazine by either boiling dilute sulphuric acid or hydrochloric acid at the ordinary temperature yields a product showing all the physical properties of carvenone with the exception of a slight lævo-rotation, apparently due to admixture of a small quantity of an intermediate compound in the hydrolysis.

l-*Carane*, $C_{10}H_{18}$, has b. p. 169—169·5°/761 mm., D_0^{20} 0·8411, n_D 1·4569, $[\alpha]_D$ −47·06°, is very stable towards permanganate, and combines, with generation of heat, with halogen hydracids and bromine. The *bromo*-derivative, $C_{10}H_{19}Br$, obtained by the action of hydrobromic acid, has D_0^{20} 1·1774, n_D 1·4910, $[\alpha]_D$ −6·40°, and yields $\Delta^{8(9)}$-*m*-menthene and $\Delta^{3(8)}$-*m*-menthene in the same way as *d*-carane (*loc. cit.*). T. H. P.

Refutation of Bülow's Views Concerning Pyrazoline-carboxylic Acids. EDUARD BUCHNER (*Ber.*, 1912, 45, 117—121).—Many arguments are advanced to disprove Bülow's view (this vol., i, 134) that a mixed azine, $CHX:N\cdot N:CX\cdot CH_2X$, not a pyrazoline derivative, $N<\begin{matrix}CX-CHX \\ NH\cdot CHX\end{matrix}$, is produced by the action of ethyl diazo-acetate on an unsaturated ester of the type $CHX:CHX$ ($X = CO_2Et$). C. S.

Derivatives and Decomposition Products of Methyl Methoxy-benzoylacetates. ANDRÉ WAHL and C. SILBERZWEIG (*Bull. Soc. Chim.*, 1912, [iv], 11, 61—69).—The methoxybenzoylacetates are convertible into $\alpha\beta$-diketonic esters, and, as these may react with various reagents giving compounds identical with those obtainable from the initial β-ketonic esters, the following compounds have been prepared and characterised so that they may be readily identified.

Methyl α-oximino-o-methoxybenzoylacetate,

$$OMe\cdot C_6H_4\cdot CO\cdot C(NOH)\cdot CO_2Me,$$

m. p. 146—147°, produced by the action of nitrous acid on the β-ketonic ester in acetic acid, crystallises from ether. The original ester reacts with phenylhydrazine to form Tahara's 1-phenyl-3-*o*-methoxyphenyl-5-pyrazolone, $PhN<\begin{matrix}N{=}C\cdot C_6H_4\cdot OMe \\ CO\cdot CH_2\end{matrix}$, m. p. 133—134°, yellow needles, and with *p*-nitrophenylhydrazine to form 1-p-*nitrophenyl*-3-o-*methoxyphenyl*-5-*pyrazolone*, m. p. 217—218°, brown needles.

Methyl α-phenylhydrazonoazo-o-methoxybenzoylacetate,

$$OMe\cdot C_6H_4\cdot CO\cdot C(:N\cdot NHPh)\cdot CO_2Me,$$

m. p. 138—139°, obtained by the action of benzenediazonium chloride on the ester in the cold, forms yellow crystals from alcohol, and reacts with phenylhydrazine to form 4-*phenylhydrazono*-1-*phenyl*-3-o-*methoxyphenyl*-5-*pyrazolone*, m. p. 139°, orange crystals, and with *p*-nitrophenylhydrazine to form 4-*phenylhydrazono*-1-p-*nitrophenyl*-3-o-*methoxyphenyl*-5-*pyrazolone*, m. p. 200°, red crystals, from pyridine.

Methyl p-*nitrophenylhydrazono*-o-*methoxybenzoylacetate*, m. p. 170°, obtained by the action of the sodium derivative of *p*-nitrophenylnitrosoamine on the β-ketonic ester, forms yellow crystals, and reacts with phenylhydrazine to give 4-p-*nitrophenylhydrazono*-1-*phenyl*-3-o-*methoxyphenyl*-5-*pyrazolone*, m. p. 267°, red crystals.

Methyl oximino-m-*methoxybenzoylacetate*, m. p. 115—116°, forms colourless needles from ether and light petroleum, and on treatment with phenylhydrazine gives 4-*oximino*-1-*phenyl*-3-m-*methoxyphenyl*-5-*pyrazolone*, m. p. 157°, which forms red crystals from acetic acid.

Methyl phenylhydrazono-m-*methoxybenzoylacetate*, m. p. 72—73°, forms yellow crystals; the free *acid*, m. p. 118—120°, forms yellow needles. *Methyl* p-*nitrophenylhydrazono*-m-*methoxybenzoylacetate*, m. p. 155—156°, crystallises in yellow needles. 1-*Phenyl*-3-m-*methoxyphenyl*-5-*pyrazolone*, m. p. 124°, forms pale yellow crystals. 4-*Phenylhydrazono*-1-*phenyl*-3-m-*methoxyphenyl*-5-*pyrazolone*, m. p. 137°, and the corresponding 4-p-*nitrophenylhydrazone*, m. p. 235°, both form red crystals.

Methyl oximinoanisoylacetate, m. p. 154°, forms colourless crystals from boiling methyl alcohol.

Methyl phenylhydrazonoanisoylacetate, m. p. 121—122°, forms orange crystals; the *free acid*, m. p. 149—150°, is yellow. The *acetyl* derivative of the ester has m. p. 116°, crystallises in colourless needles, and on reduction furnishes some acetanilide, whence it is believed to have the constitution $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}C(:N{\cdot}NPhAc){\cdot}CO_2Me$ (compare Auwers, Abstr., 1909, i, 222).

Methyl p-*nitrophenylhydrazonoanisoylacetate*, m. p. 175°, forms yellow crystals; the *free acid*, m. p. 236—238°, is also yellow, but dissolves in alkalis with an intense red colour.

1-*Phenyl*-3-p-*methoxyphenyl*-5-*pyrazolone* has m. p. 137—138°; the 4-*oximino*-derivative, m. p. 244°, forms red crystals. p-*Nitrophenyl*-3-p-*methoxyphenyl*-5-*pyrazolone*, m. p. 204—205°, is brown. 4-*Phenylhydrazono*-1-*phenyl*-3-p-*methoxyphenyl*-5-*pyrazolone*, m. p. 177°, is red; the corresponding p-*nitrophenylhydrazone*, m. p. 213—214°, separates from acetic acid in violet crystals, and the isomeric 4-*phenylhydrazono*-1-p-*nitrophenyl*-3-p-*methoxyphenyl*-5-*pyrazolone*, m. p. 239°, is red.

The methoxybenzoylacetic esters are hydrolysed by boiling with 20% sulphuric acid into the corresponding *o*-, *m*-, and *p*-methoxyacetophenones. The semicarbazone of *m*-methoxyacetophenone has m. p. 195—197° (compare Klages, Abstr., 1904, i, 45) and that of the *p*-compound melts at 197°. T. A. H.

Quinazolines. XXVIII. 4-Quinazolone-2-phthalones and Certain of their Derivatives. Marston T. Bogert and Michael Heidelberger (*J. Amer. Chem. Soc.*, 1912, **34**, 183—201).—An account is given of certain phthalones obtained by the action of

phthalic anhydride on 2-methyl-4-quinazolone (2-methyl-4-hydroxyquinazoline) and its derivatives. These compounds, like the quinophthalones, behave as yellow dyes, but are inferior to the latter in tinctorial power.

4-*Quinazolone-2-phthalone* [4-*hydroxyquinazoline-2-phthalone*, 2-*indandionyl-4-quinazolone*, or β-(4′-*quinazolonyl-2′*)-*diketohydrindene*], $\begin{matrix} C_6H_4\cdot N \\ | \\ CO\text{-}NH \end{matrix}\!\!>\!C\cdot CH\!<\!\begin{matrix} CO \\ CO \end{matrix}\!>\!C_6H_4$, m. p. 318° (corr.), obtained by heating a mixture of 2-methyl-4-quinazolone and phthalic anhydride to about 200°, forms pale yellow, prismatic needles or hexagonal plates, and when heated above 200° sublimes in woolly masses of minute needles. In one experiment in which a large excess of phthalic anhydride was used, on extracting the reaction product with hot water, 2-*methyl-4-quinazolone phthalate* was obtained, which crystallises in pale yellow, fluorescent needles with $1H_2O$; the anhydrous salt has m. p. 171° (corr.). The *di-sodium* salt of the phthalone is orange-red, whilst the *mono-sodium* and *silver* salts are pale yellow. On reducing the phthalone with zinc dust and sodium hydroxide, 4-*quinazolone-2-hydrindone*, $C_6H_4\!<\!\begin{matrix} N{=}C{-}CH\cdot CH_2 \\ CO\!:\!NH\ CO{-}C_6H_4 \end{matrix}$, is obtained, which forms olive-yellow, microscopic crystals, sublimes above 160°, and melts at about 328° (decomp.). When the phthalone is heated with aniline in presence of zinc chloride, the *anil*,

$$\begin{matrix} C_6H_4\cdot N \\ | \\ CO\text{-}NH \end{matrix}\!\!>\!C\cdot CH\!<\!\begin{matrix} CO\text{———} \\ C(NPh) \end{matrix}\!>\!C_6H_4,$$

m. p. 284—285° (uncorr.), is produced, which crystallises in brilliant, scarlet needles; its *sodium* salt and *compound* with zinc chloride are described. From the product of this reaction, a small quantity of another *anil*, m. p. 258°, was obtained, which forms red crystals and appears to be a condensation product of 1 mol. of aniline with 2 mols. of the phthalone. 4-*Quinazolone-2-phthalonemonophenylhydrazone*, m. p. about 225° (uncorr.), was obtained as an orange-brown, microcrystalline powder. 4-*Quinazolone-2-phthalone-6-sulphonic acid*, m. p. about 355—360° (uncorr.), crystallises in minute plates or needles; its *mono-* and *di-sodium* and *barium* salts are described. Solutions of the di-sodium salt dye wool or silk light yellow shades. By the action of bromine on the sulphonic acid, there were formed a di- and a pentabromo-2-methyl-4-quinazolone, a bromo-2-methyl-4-quinazolonesulphonic acid, phthalic acid, and sulphuric acid. *Dibromo-2-methyl-4-quinazolone*, m. p. about 293° (decomp.), forms masses of delicate, colourless needles. *Pentabromo-2-methyl-4-quinazolone*, m. p. about 243·5° (decomp.), crystallises in colourless, prismatic needles. *Bromo-2-methyl-4-quinazolonesulphonic acid*, m. p. 285—286·5° (uncorr.), forms a grey, amorphous solid containing $1H_2O$; its *barium* salt crystallises with $4\frac{1}{2}H_2O$.

Attempts to prepare 4-quinazolone-2-phthalines by heating the ammonium salt of the phthalone with alcoholic ammonia in sealed tubes did not meet with success. *Bis-(4-quinazolone-2)-β-phthaline*, $C_8H_5ON_2\cdot CH\!:\!C\!<\!\begin{matrix} NH \\ C_6H_4 \end{matrix}\!>\!C\!:\!CH\cdot C_8H_5ON_2$, obtained by heating a

mixture of phthalimide and 2-methyl-4-quinazolone, is an orange-brown substance which darkens gradually when heated; its solution in dilute acetic acid acts as a powerful yellow dye. 4-*Quinazolone-2-β-phthaline*, $C_8H_5ON_2·CH:C<\begin{smallmatrix}CO-\\NH\end{smallmatrix}>C_6H_4$, m. p. about 349° (decomp.), is also produced in this reaction, and forms orange-brown, microscopic prisms.

2-Methyl-4-quinazolone reacts with succinic anhydride with production of a tarry mass, from which a small quantity of a *substance*, m. p. 274—277° (decomp.), was isolated in the form of thin, colourless, lustrous plates.

6-*Nitro*-4-*quinazolone*-2-*phthalone*, obtained by heating 6-nitro-2-methyl-4-quinazolone with phthalic anhydride at about 210°, forms minute, yellow crystals and does not melt below 355°.

7-*Acetylamino*-4-*quinazolone*-2-*phthalone*, resulting from the action of phthalic anhydride on 7-acetylamino-2-methyl-4-quinazolone, crystallises in bright yellow, lustrous plates, and does not melt below 356°.

2-*Methyl*-3-*ethyl*-4-*quinazolone*, $C_6H_4<\begin{smallmatrix}N{=}CMe\\CO·NEt\end{smallmatrix}$, m. p. 67° (corr.), obtained by heating acetylanthranil with excess of an aqueous solution of ethylamine in presence of a little potassium hydroxide, forms colourless, slender needles; its *platinichloride* decomposes at about 229°. In one experiment in which potassium hydroxide was not added, *anthranilethylamide*, $NHEt·CO·C_6H_4·NHAc$, m. p. 139·5—140·5° (corr.), was isolated in the form of transparent, prismatic plates.

3-*Ethyl*-4-*quinazolone*-2-*phthalone*, m. p. 198·5° (corr.), obtained from 2-methyl-3-ethyl-4-quinazolone and phthalic anhydride, forms bright yellow, lustrous, prismatic needles with a slight green fluorescence.

E. G.

Formation of Pyrimidines by Use of Nitromalonaldehyde. WILLIAM J. HALE and HARVEY C. BRILL (*J. Amer. Chem. Soc.*, 1912, **34**, 82—94).—Hill and Torrey (Abstr., 1899, i, 788) have shown that nitromalonaldehyde reacts readily with primary amines. This work has now been extended to other amino-compounds.

When carbamide is allowed to react with the sodium derivative of nitromalonaldehyde in presence of a few drops of piperidine, the mono-ureide and 5-nitro-2-hydroxypyrimidine are produced.

Nitromalonaldehyde mono-ureide, $NH_2·CO·N:CH·CH(NO_2)·CHO$, m. p. 154° (corr.), forms pale yellow crystals; its *sodium* salt crystallises with $3H_2O$. The *anil*,

$$NH_2·CO·N:CH·CH(NO_2)·CH:NPh,$$

m. p. 211° (corr.), crystallises in lustrous, red needles. The *oxime*, $NH_2·CO·N:CH·CH(NO_2)·CH:NOH$, m. p. 174—175° (corr.), forms yellow leaflets.

5-*Nitro-2-hydroxypyrimidine*, $OH·C<\begin{smallmatrix}N·CH\\N:CH\end{smallmatrix}>C·NO_2$, m. p. 203·5° (corr.), crystallises in small, yellow plates; the *sodium*, *potassium*,

barium, and *silver* salts are described. The *methyl ether*, m. p. 168—169° (corr.), forms colourless plates.

5-*Nitro-2-phenylpyrimidine*, $CPh<\substack{N\cdot CH \\ N:CH}>C\cdot NO_2$, m. p. 219° (corr.), obtained by the interaction of benzamidine hydrochloride and sodium nitromalonaldehyde, crystallises in white plates.

5-*Nitro*-2-*aminopyrimidine*, $NH_2\cdot C<\substack{N\cdot CH \\ N:CH}>C\cdot NO_2$, m. p. 236° (corr.), prepared by the action of guanidine carbonate on sodium nitromalonaldehyde, forms colourless, slender needles, and when heated with solution of alkali hydroxide is converted into 5-nitro-2-hydroxypyrimidine; the *acetyl* derivative,

$$NHAc\cdot C<\substack{N\cdot CH \\ N:CH}>C\cdot NO_2,$$

m. p. 172·5° (corr.), crystallises in long, colourless needles. When a small quantity of potassium hydroxide is added to a mixture of 5-nitro-2-aminopyrimidine and carbon disulphide at 60°, 5 : 5′-*dinitro*-2 : 2′-*dipyrimidylthiocarbamide*, $CS[NH\cdot C<\substack{N\cdot CH \\ N:CH}>C\cdot NO_2]_2$, m. p. 230—231° (corr.), is produced, which forms a mass of glistening leaflets.

Nitromalonaldehyde phenylureide, $CHO\cdot CH(NO_2)\cdot CH:N\cdot CO\cdot NHPh$, m. p. 176—177° (corr.), was obtained by the condensation of nitromalonaldehyde with phenylcarbamide. The corresponding *benzylureide*, m. p. 150—151° (corr.), and *methylureide* were also prepared.

E. G.

Chlorides of Amino-acids. CARL MANNICH and R. KUPHAL (*Ber.*, 1912, **45**, 314—322).—By the internal condensation of benzylaminoacetyl chloride and of similar amino-acid chlorides in the presence of aluminium chloride, the authors hoped to prepare derivatives of *iso*quinoline, $CH_2Ph\cdot NH\cdot CH_2\cdot COCl \longrightarrow C_6H_4<\substack{CH_2\cdot NH \\ CO-CH_2}$. It was found, however, that the chlorides readily lost hydrogen chloride even in the absence of aluminium chloride with the formation of diketopiperazines.

Ethyl benzylaminoacetate, prepared by the interaction of ethyl chloroacetate and benzylamine, is a colourless liquid of aromatic odour, b. p. 153—154°/13 mm., and is readily hydrolysed by hydrochloric acid to benzylaminoacetic acid (Mason and Winder, Trans., 1894, **67**, 187). It is accompanied by a substance, which crystallises from dilute alcohol in lustrous, white leaflets, m. p. 238—239°, consisting probably of *benzylaminoacetobenzylamide hydrochloride*,

$$C_7H_7\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7,HCl.$$

The amino-acid is converted by the action of phosphorus pentachloride and acetyl chloride (Fischer, Abstr., 1905, i, 263) into *benzylaminoacetyl chloride hydrochloride*, $C_7H_7\cdot NH\cdot CH_2\cdot COCl,HCl$, which forms slender, white needles, and when heated in nitrobenzene solution yields 3 : 6-*diketo*-1 : 4-*dibenzylpiperazine*, $C_7H_7\cdot N<\substack{CH_2\cdot CO \\ CO\cdot CH_2}>N\cdot C_7H_7$, crystallising in white needles, m. p. 172—173°.

3:4-*Methylenedioxybenzylamine*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}NH_2$, prepared by reducing piperonaldoxime with sodium amalgam and alcohol, the solution being maintained continually acid by the addition of acetic acid, is a colourless liquid, b. p. 138—139°/13 mm.; on exposure to air it forms a solid *carbonate*; the *hydrochloride*, lustrous, white leaflets, has m. p. 227°; the *benzoyl* and *chloroacetyl* derivatives crystallise in slender, white needles, m. p. 117—118° and 107—108° respectively. It reacts with ethyl chloroacetate, yielding *ethyl* 3 : 4-*methylenedioxybenzylaminoacetate*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, which forms a *hydrochloride*, white needles, m. p. 157—158°, and is hydrolysed by aqueous potassium hydroxide to the corresponding *acid*. This has m. p. 206—207°, and is converted by acetyl chloride and phosphorus pentachloride into 3 : 4-*methylenedioxybenzylaminoacetylchloride hydrochloride*, $C_{10}H_{11}O_3NCl_2$.

3 : 6-*Diketo*-1 : 4-*di*-(3′ : 4′)-*methylenedioxybenzylpiperazine*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}N{<}{\begin{matrix}CH_2{\cdot}CO\\CO{\cdot}CH_2\end{matrix}}{>}N{\cdot}CH_2{\cdot}C_6H_3{:}O{:}CH_2,$$

prepared by heating the preceding chloride hydrochloride in nitrobenzene solution, forms white needles, m. p. 234—235°.

Ethyl benzylmethylaminoacetate, $C_7H_7{\cdot}NMe{\cdot}CH_2{\cdot}CO_2Et$, obtained from ethyl chloroacetate and benzylmethylamine, has b. p. 138°/13 mm.; the syrupy *hydrochloride*, the orange *platinichloride*, and the *picrate*, crystallising in stout, yellow needles, m. p. 122—123°, are described. When hydrolysed with concentrated hydrochloric acid, it yields the corresponding *acid*, $C_{10}H_{13}O_2N$, which forms a *hydrochloride*, sintering at 174°, m. p. 180—181°, and a *chloride hydrochloride*, $C_7H_7{\cdot}NMe{\cdot}CH_2{\cdot}COCl,HCl$.

The latter compound reacts with aluminium chloride at 100°, yielding carbon monoxide, formaldehyde, and benzylmethylamine, together with s-*dibenzyldimethylmethylenediamine*, $CH_2(NMe{\cdot}C_7H_7)_2$, a pale yellow oil, b. p. 172—175°/8 mm. The constitution of the last-named compound has been established by its synthesis from benzylmethylamine and formaldehyde. F. B.

Preparation of Halogenated Dehydroindigotin Salts, their Nuclear Homologues and Substitution Products. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 239314).—Halogenated dehydroindigotin salts have previously been described, and the preparation of higher halogenated derivatives is now recorded.

Trichlorodehydroindigotin acetate, a canary-yellow powder, is prepared by passing chlorine into a cooled acetic acid solution of dehydroindigotin acetate until the product has completely separated; when nitrobenzene is employed as solvent, a *tetrachlorodehydroindigotin hydrochloride* is obtained, whilst under these conditions indigotin yields *trichlorodehydroindigotin hydrochloride* (isolated in the form of its *bisulphite* compound), and 5 : 5′-dibromoindigotin in acetic acid solution furnishes *dichlorodibromodehydroindigotin hydrochloride*. Other solvents, such as acetyl chloride or carbon tetrachloride, can be employed, and the formation of other halogenated indigotins is discussed. F. M. G. M.

Action of Alkyloxides and Amines on Benzoyl *iso*Cyanochloride [Benzoylcarbylamine Chloride]. TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1912, **34**, 164—170).—Benzoylcarbylamine chloride, $C_6H_5 \cdot CO \cdot N:CCl_2$, obtained by Johnson and Menge (Abstr., 1904, i, 949) by the action of chlorine on benzoyl thiocyanate, is decomposed by water with formation of hydrochloric acid, benzamide, and benzoic acid. It combines with sodium alkyloxides to form compounds of a new class, the acylimidocarbonates, and reacts with amines with production of substituted guanidines, which yield stable salts with mineral acids and are hydrolysed by alkali hydroxide with formation of the free guanidines and benzoic acid.

Diethyl benzoylimidocarbonate, $NBz:C(OEt)_2$, b. p. 93—100°/20 mm. and 110—120°/32 mm., was prepared by the action of benzoylcarbylamine chloride on sodium ethoxide. *Dimethyl benzoylimidocarbonate*, b. p. 95—102°/20 mm., is a colourless oil.

Benzoyl-aγ-diphenylguanidine, $NBz:C(NHPh)_2$, m. p. 212° (decomp.), obtained by the action of benzoylcarbylamine chloride on a solution of aniline in benzene, forms colourless needles. *β-Benzoyl-aγ-di*-o- and -m-*tolylguanidines*, $NBz:C(NH \cdot C_6H_4Me)_2$, have m. p. 126° and 177—178° respectively. *Di*-m-*tolylguanidine*, $NH:C(NH \cdot C_6H_4Me)_2$, m. p. 108—109°, was obtained from the benzoyl compound by hydrolysis with potassium hydroxide. *β-Benzoyl-aγ-di*-p-*tolylguanidine*, m. p. 190°, yields a *hydrochloride*, m. p. 190—191° (decomp.). The following guanidines were also prepared: *benzoyltetraphenylguanidine*, m. p. 142—144°; *β-benzoyl-aγ-diphenyl-aγ-dimethylguanidine*, m. p. 135°; *β-benzoyl-aγ-di*-p-*anisylguanidine*, m. p. 128°, and *di*-p-*anisylguanidine*, m. p. 153°; *β-benzoyl-aγ-di-β-naphthylguanidine*, m. p. 162°, and *di-β-naphthylguanidine*, m. p. 197° (decomp.). E. G.

Reduction of Semicarbazones. SIDONIUS KESSLER and HANS RUPE (*Ber.*, 1912, **45**, 26—30).—Semicarbazones are readily reduced by sodium amalgam in dilute alcoholic solution at a slightly elevated temperature. In some instances, for example, those of cinnamaldehyde and styryl methyl ketone, the influence of the constitution of the semicarbazone prevents reduction to semicarbazide.

Benzylsemicarbazide, $CH_2Ph \cdot NH \cdot NH \cdot CO \cdot NH_2$, from benzaldehyde-semicarbazone, crystallises in lustrous platelets, m. p. 155°. It is distinctly basic, dissolving in cold dilute acids, and reduces Fehling's solution on boiling. The *hydrochloride* forms silky, lustrous needles, m. p. 178—180°; the *sulphate* yields slender needles, m. p. 158°; the *picrate* gives slender, yellow needles, m. p. 161—162°, and the *oxalate* has m. p. 178—179° (decomp.). The *acetyl* derivative crystallises in beautiful, colourless plates, m. p. 207°; a diacetate could not be obtained; the *benzoyl* derivative forms colourless needles, m. p. 230°.

Nitrosobenzylsemicarbazide, $CH_2Ph \cdot N(NO) \cdot NH \cdot CO \cdot NH_2$, prepared by the action of sodium nitrite and hydrochloric acid on benzylsemicarbazide, crystallises in long needles, m. p. 133° (decomp.).

p-*Methylbenzylsemicarbazide* crystallises in slender, colourless needles, m. p. 158°; the *hydrochloride* forms colourless needles, m. p. 138° (decomp.); the *sulphate* decomposes at 187°; the *picrate* yields yellow needles, m. p. 178° (decomp.), and the acid *oxalate* decomposes at

175°. The *acetyl* derivative crystallises in glistening, colourless platelets, m. p. 225° (not decomp.).

Nitroso-p-*methylbenzylsemicarbazide* separates in colourless platelets, and decomposes at 126—127°.

When cinnamaldehydesemicarbazone is reduced, β-phenylpropaldehydesemicarbazone, m. p. 128°, is the sole product.

Similarly, from the semicarbazone of styryl methyl ketone, the product is the semicarbazone of phenylethyl methyl ketone.

E. F. A.

Reduction of Semicarbazones and the Preparation of Some Hydroxytriazoles. HANS RUPE and E. OESTREICHER (*Ber.*, 1912, **45**, 30—38. Compare preceding abstract).—The property of semicarbazones of being reduced to semicarbazide is closely dependent on their constitution. A phenyl residue must be attached directly to the group C⁚N. Aliphatic hydrocyclic and compounds in which phenyl is replaced by benzyl cannot be reduced. The semicarbazones of benzoylpropionic acid and of *p*-benzoquinone could not be reduced. The semicarbazides vary considerably in their basic properties; those from benzophenone, acetophenone, and deoxybenzoin dissolve in dilute acids in the cold, whereas those from salicylaldehyde or piperonal dissolve only when boiled with acids.

3 : 4-*Methylenedioxybenzylsemicarbazide*,

$$CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

from piperonalsemicarbazone, forms transparent prisms, m. p. 184°. The *acetyl* derivative crystallises in slender, transparent needles, m. p. 203—204°; the *formyl* derivative forms long, transparent, rhombic plates, m. p. 204—205°.

3-*Hydroxy*-(mp-*methylenedioxybenzyl*)-5-*methyl*-1 : 2 : 4-*triazole*,

$$CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}N{<}\begin{matrix}CMe{:}N\\ \vert\\ NH{-}CO\end{matrix},$$

prepared by boiling the acetyl derivative with 30% sodium hydroxide and decomposing the sodium salt formed with hydrochloric acid, forms opaque, square crystals with stunted ends, m. p. 190°; it forms characteristic metallic salts. From the formyl derivative of the semicarbazide, 3-*hydroxy*-(mp-*methylenedioxybenzyl*)-1 : 2 : 4-*triazole* is obtained; it crystallises in stout, transparent plates, m. p. 246—247°. α-*Phenylethylsemicarbazide*, $CHMePh{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, from acetophenonesemicarbazone, crystallises in four-edged, transparent prisms, m. p. 142—143°. The *acetyl* derivative forms platelets, m. p. 228—230°, the *formyl* derivative crystallises in slender, matted needles, m. p. 187°

3-*Hydroxy*-1-α-*phenylethyl*-5-*methyltriazole*,

$$CHMePh{\cdot}N{<}\begin{matrix}CMe{:}N\\ \vert\\ N{=\!=}C{\cdot}OH\end{matrix},$$

crystallises in short, well formed prisims, m. p 146—147°.

3-*Hydroxy*-1-α-*phenylethyltriazole* is obtained in transparent, slender, intergrown prisms, m. p. 140°.

Diphenylmethylsemicarbazide, $CHPh_2{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, crystallises in long, lustrous, transparent needles, m. p. 164—165°; it gives an

intense yellow coloration with concentrated sulphuric acid. The *acetyl* derivative crystallises in small, transparent prisms, m. p. 237°; the *formyl* derivative yields small, colourless needles, m. p. 182°. The *nitrosoamine*, $CHPh_2\cdot N(NO)\cdot NH\cdot CO\cdot NH_2$, forms slender, faintly yellow-coloured needles, m. p. 122°.

3-*Hydroxy*-1-*diphenylmethyl*-5-*methyltriazole*, $CHPh_2\cdot N\!\!<\!\!\begin{array}{l}CMe{:}N \\ \quad\;\;\; | \\ N{=\!=}C\cdot OH\end{array}$, crystallises in glistening needles, which appear under the microscope as prisms with two superposed pyramids.

3-*Hydroxy*-1-*diphenylmethyltriazole* forms slender, matted needles, m. p. 253°.

αβ-Diphenylethylsemicarbazide, prepared from deoxybenzoinsemicarbazone, crystallises in long, slender, transparent needles grouped in stellar aggregates, m. p. 139°. The *acetyl* derivative forms slender, woolly needles, m. p. 196°; the *formyl* derivative gives small, transparent prisms, m. p. 194°.

o-*Hydroxybenzylsemicarbazide*, from salicylaldehydesemicarbazone, crystallises in four-edged prisms, m. p. 128°. The *acetyl* derivative separates in slender needles, m. p. 204°; the *formyl* derivative forms flat, transparent plates, m. p. 183—184°.

3-*Hydroxy*-1-o-*hydroxybenzyl*-5-*methyltriazole* forms crystals, m. p. 192°, and gives a reddish-violet coloration with sulphuric acid.

3-*Hydroxy*-1-o-*hydroxybenzyltriazole* forms platelets of silvery lustre, m. p. 211° (decomp.).

3-*Hydroxy*-5-*benzyl*-1-*methyltriazole* crystallises in transparent prisms, m. p. 168°.

3-*Hydroxy*-1-*benzyltriazole* forms lustrous, nacreous platelets, m. p. 147—148°. E. F. A.

Determination of Configuration of Stereoisomeric Hydrazones. MAX BUSCH (*Ber.*, 1912, **45**, 73—85).—Stereoisomeric diphenylsemicarbazones of unsymmetrical esters of dithiocarbonic acid, $NHPh\cdot CO\cdot NPh\cdot N{:}C(SR)\cdot SR'$, analogous to the stereoisomeric phenylhydrazones (Abstr., 1911, i, 811) have been obtained.

Ethyl dithiocarbonate-diphenylsemicarbazide,

$$NHPh\cdot CO\cdot NPh\cdot NH\cdot CS_2Et,$$

stout needles, m. p. 149—150°, obtained from equal molecular quantities of phenylcarbimide and ethyl phenyldithiocarbazinate in warm benzene, dissolves readily in aqueous alkalis, and is decomposed by prolonged boiling with alcoholic potassium hydroxide, yielding ethyl mercaptan and, after acidifying, 3-thiol-1:4-diphenyltriazolone (Abstr., 1911, i, 689). By treating its alcoholic solution with equivalent quantities of potassium hydroxide and methyl iodide, it yields (*a*) *methyl ethyl dithiocarbonate-diphenylsemicarbazone*,

$$NHPh\cdot CO\cdot NPh\cdot N{:}C(SMe)\cdot SEt,$$

m. p. 93—94°, rhombic needles. The stereoisomeric (*b*) *methyl ethyl dithiocarbonate-diphenylsemicarbazone*, m. p. 87—88°, monoclinic needles or prisms, is prepared in a similar manner from methyl dithiocarbonate-diphenylsemicarbazide, ethyl iodide, and potassium hydroxide. These

two stereoisomeric semicarbazones behave very similarly. However, when warmed at 50—60° with alcoholic potassium hydroxide, the former yields ethyl mercaptan and the methyl thio-ether of 3-thiol-1 : 4-diphenyltriazolone, whilst the latter yields methyl mercaptan and the *ethyl* thio-ether, m. p. 111—112°, of the same triazolone; in both cases the alkyl group, which was introduced first, is eliminated as a mercaptan.

Another pair of stereoisomeric semicarbazones are described. *p*-Nitrobenzyl phenyldithiocarbazinate and phenylcarbimide in benzene yield p-*nitrobenzyl dithiocarbonate-diphenylsemicarbazide*,

$$NHPh{\cdot}CO{\cdot}NPh{\cdot}NH{\cdot}CS_2{\cdot}C_7H_6{\cdot}NO_2,$$

m. p. 119—120°, colourless needles, which is converted by alcoholic potassium hydroxide and methyl iodide into (*a*) p-*nitrobenzyl methyl dithiocarbonate-diphenylsemicarbazone*,

$$NHPh{\cdot}CO{\cdot}NPh{\cdot}N{:}C(SMe){\cdot}S{\cdot}C_7H_6{\cdot}NO_2,$$

m. p. 126°, stout, yellow needles. The stereoisomeric (*b*) p-*nitrobenzyl methyl dithiocarbonate-diphenylsemicarbazone*, m. p. 147°, colourless plates, is prepared in a similar manner from methyl dithiocarbonate-diphenylsemicarbazide and *p*-nitrobenzyl chloride. Either of these semicarbazones is converted, when fused or heated in alcohol for one to two hours, into an equilibrium mixture of approximately equal quantities of both forms. When warmed with alcoholic potassium hydroxide, the yellow form yields the methyl thio-ether of 3-thiol-1 : 4-diphenyltriazolone, whilst the colourless form yields methyl mercaptan and the p-*nitrobenzyl thio-ether*, m. p. 178—179°, of the same triazolone; in both cases, again, the alkyl group which was first introduced is eliminated by the action of the alkali. C. S.

Influence of the Acridine Ring on the Colour of Certain Colouring Matters. A. E. Porai-Koschitz, Y. I. Auschkap, and N. K. Amsler (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1587—1603).—In order to decide between the chromophore and dynamic theories (compare von Baeyer, Abstr., 1907, i, 757) of the colour of triphenylmethane colouring matters, the authors have prepared and studied acridylmalachite-green and acridylpyronine. The results obtained are distinctly in favour of the latter of the two hypotheses, since the absorption spectra of the two colouring matters scarcely differ from those of malachite-green and rosamine, the absorption bands being displaced towards the red end of the spectrum to an extent approximately such as is usually observed with any more or less considerable increase in the molecular weight. A further consequence of the replacement of the benzene ring by an acridine nucleus consists in a marked diminution in the "permanency" of the spectral bands, this being expressed in a decrease in the dyeing properties of the colouring matters. In the case of acridylmalachite-green, the quinonoid base was obtained in the pure state.

The action of 5-aldehydoacridine (compare Abstr., 1911, i, 688) on dimethylaniline in presence of zinc chloride and subsequent treatment with dilute hydrochloric acid, followed by oxidation of any leuco-compound with lead dioxide, yield a small quantity of a violet colour-

ing matter, which was not investigated further, and *dimethylaminophenylacridylmethylenequinonodimethylimonium chloride*,

$$N{<}^{C_6H_4}_{C_6H_4}{>}C{\cdot}C{<}^{C_6H_4{:}NMe_2Cl}_{C_6H_4{\cdot}NMe_2},$$

which is a green colouring matter with a bronze lustre, dissolving slightly in water and readily in alcohol. It dyes cotton a somewhat bluer green than malachite-green, whilst wool is dyed only very faintly in neutral solution, but more strongly in presence of borax or ammonia. The first portions of wool immersed are coloured green with a slight blue tinge, but if successive portions are introduced into the same bath, the colour approaches more and more nearly to blue; this is found to be a result of the presence of alkali.

Tetramethyldiaminodiphenylacridylmethane (leuco-base of acridylmalachite-green), $N{<}^{C_6H_4}_{C_6H_4}{>}C{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, forms yellow, acicular crystals, m. p. 171—172°, insoluble in water, but readily soluble in acids or organic solvents.

The *quinonoid base*, $N{<}^{C_6H_4}_{C_6H_4}{>}C{\cdot}C{<}^{C_6H_4{:}NMe_2{\cdot}OH}_{C_6H_4{\cdot}NMe_2}$, forms greenish-golden plates.

In neutral aqueous solution the maximum intensity of the absorption band of acridylmalachite-green lies at $\lambda = 642\ \mu\mu$, whilst, according to Formanek, that for malachite-green is at $\lambda = 618{\cdot}5\ \mu\mu$; the displacement caused by the substitution of an acridine nucleus for a benzene ring is hence $23{\cdot}5\ \mu\mu$.

Acridylpyronine, $N{<}^{C_6H_4}_{C_6H_4}{>}C{\cdot}C{<}^{C_6H_3(NEt_2)}_{C_6H_3({:}NEt_2{\cdot}OH)}{>}O$, obtained by condensing 5-aldehydoacridine with *m*-diethylaminophenol in presence of sulphuric acid, dissolves in very dilute acids, giving a violet-red colour, changing to cherry-red on addition of concentrated acid. It dyes silk and wool reddish-violet, and cotton blue with a red tinge, no mordant being necessary. The absorption bands are almost identical in aqueous and in alcoholic solution, and in both cases little change is produced by acidification with nitric acid or addition of potassium hydroxide; this behaviour is characteristic of all colouring matters of the pyronine series. The absorption spectrum of acridine lies in the ultra-violet, close to the visible part of the spectrum, and the introduction of the pyronine residue results in the displacement of this absorption into the violet. The maximum intensities of the absorption bands lie at 580 $\mu\mu$ and $534{\cdot}8\ \mu\mu$, whilst Biehringer (Abstr., 1897, i, 73) found for tetra-ethylrosamine, $563{\cdot}5$ and $527{\cdot}5\ \mu\mu$; the displacements caused by the replacement of the benzene ring by an acridine residue are hence $16{\cdot}5\ \mu\mu$ and $7{\cdot}3\ \mu\mu$. T. H. P.

Relation between Constitution and Phototropy. MAURIZIO PADOA and F. BOVINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 712—717. Compare Padoa and Graziani, Abstr., 1910, i, 778; Padoa and Santi, Abstr., 1911, i, 693, 1029).—The phototropy of the compounds described in the present paper follows the regularities previously discovered.

β-Benzil-α-naphthylosazone, $C_2Ph_2({:}N{\cdot}NH{\cdot}C_{10}H_7)_2$, obtained by

Purgotti's method (Abstr., 1893, i, 354), forms lemon-yellow crystals, m. p. 175°, and is not phototropic.

β-Piperil-α-naphthylosazone, $C_2(C_6H_3{:}O_2{:}CH_2)_2({:}N{\cdot}NH{\cdot}C_{10}H_7)_2$, prepared by MacNair's method (Abstr., 1890, 1245), crystallises in yellow needles, m. p. 189°, and is prototropic.

β-Anisil-α-naphthylosazone, $C_2(C_6H_4{\cdot}OMe)_2({:}N{\cdot}NH{\cdot}C_{10}H_7)_2$, prepared like the preceding compound, crystallises in golden-yellow needles, m. p. 155°, and is prototropic.

Piperonaldehyde-α-naphthylhydrazone,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}N{\cdot}NH{\cdot}C_{10}H_7,$$

crystallises in greenish-yellow needles, m. p. 147°, and is not phototropic.

Salicylaldehyde-α-naphthylhydrazone, $HO{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NH{\cdot}C_{10}H_7$, forms lustrous, golden-yellow needles, m. p. 134°, and is not phototropic.

Vanillin-α-naphthylhydrazone, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}N{\cdot}NH{\cdot}C_{10}H_7$, is an unstable, yellow, crystalline powder, which is not phototropic.

p-*Tolualdehyde-α-naphthylhydrazone*, $C_6H_4Me{\cdot}CH{:}N{\cdot}NH{\cdot}C_{10}H_7$, crystallises in greenish-yellow needles, m. p. 152°, and is not phototropic.

β-Benzil-1 : 3 : 4-*xylylosazone*, $C_2Ph_2({:}N{\cdot}NH{\cdot}C_6H_3Me_2)_2$, is an orange-yellow, crystalline substance, m. p. 71—72°, and is phototropic.

Piperil-1 : 3 : 4-*xylylosazone*, $C_2(C_6H_3{:}O_2{:}CH_2)_2({:}N{\cdot}NH{\cdot}C_6H_3Me_2)_2$, forms lemon-yellow prisms, m. p. 187°, and is phototropic.

Anisil-1 : 3 : 4-*xylylosazone*, $C_2(C_6H_3{\cdot}OMe)_2({:}N{\cdot}NH{\cdot}C_6H_3Me_2)_2$, is an orange-yellow, crystalline substance, m. p. 75°, and is phototropic.

Cuminil-1 : 3 . 4-*xylylosazone*, $C_2(C_6H_4Pr^\beta)_2({:}N{\cdot}NH{\cdot}C_6H_3Me_2)_2$, is a yellow, crystalline substance, m. p. 64—70°, and is not phototropic.

R. V. S.

Researches on Purines. IV. 2-Oxypurine and 2-Oxy-8-methylpurine. Carl O. Johns (*J. Biol. Chem.*, 1912, 11, 67—72).—6-Oxypurine (hypoxanthine) was first isolated by Scherer in 1850, and nearly fifty years later was synthesised by Fischer. 8-Oxypurine was prepared by Fischer and Ach. 2-Oxypurine was prepared by Tafel and Ach from guanine, but they did not offer any proof of its structure. In the present research it was prepared from 5 : 6-diamino-2-pyrimidone, and the product agrees in all respects with that of Tafel and Ach. When 5 : 6-diamino-2-pyrimidone is heated with formic acid, a *monoformyl* derivative is obtained; this yields a potassium salt, which when heated gives off water, and changes to the potassium salt of 2-oxypurine; 2-oxypurine crystallises with $1H_2O$, and does not lose it until heated to 120°. The picrate, nitrate, and hydrochloride were prepared.

When 5 : 6-diamino-2-pyrimidone is boiled with acetic anhydride it forms chiefly a monoacetyl compound, together with some of the diacetyl compound. When the potassium salt of the former is heated, it yields the potassium salt of 2-*oxy*-8-*methylpurine*; this substance forms a *picrate*, decomp. 250°, and a *nitrate*, decomp. 205°, which may be used for its identification.

W. D. H.

Preparation and Reactions of Azo-acyl Compounds. ROBERT STOLLÉ [with J. MAMPEL, J. HOLZAPFEL, and K. C. LEVERKUS] (*Ber.*, 1912, **45**, 273—289).—Azodiacyls of the type $R{\cdot}CO{\cdot}N{:}N{\cdot}CO{\cdot}R$ (where $R = H$, Me, $CHEt_2$, Ph, C_6H_4Cl, and α-$C_{10}H_7$) have been prepared by the action of iodine or bromine in ethereal solution on the mercury or silver salts of symmetrical diacylhydrazides,

$$R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}COR.$$

The azodiacyls prepared from hydrazides of aromatic acids are comparatively stable, whilst those derived from aliphatic acids are unstable, and could only be obtained in ethereal solution or in an impure condition as red oils. They are converted by reducing agents, such as hydriodic acid, hydrogen sulphide, and phenylhydrazine, into the original hydrazides. When treated with water they yield triacylhydrazides, the decomposition taking place according to the following scheme:

$$2N_2(CO{\cdot}R)_2 + H_2O = R{\cdot}CO_2H + N_2 + R{\cdot}CO{\cdot}NH{\cdot}N(CO{\cdot}R)_2.$$

It is supposed that the first stage in the reaction consists in the partial hydrolysis of the azodiacyl to the compound (I), which instantly decomposes, thus: (I) $NH{:}N{\cdot}CO{\cdot}R \longrightarrow H + N_2 + {\cdot}CO{\cdot}R$; this is followed by addition of H and ·COR to a second molecule of the azodiacyl with the formation of a triacylhydrazide. Evidence in support of this view is furnished by the production of triacylhydrazides by the reaction of azodibenzoyl and azodi-α-ethylbutyryl with benzaldehyde:

$$Ph{\cdot}CHO + R{\cdot}CO{\cdot}N{:}N{\cdot}CO{\cdot}R \longrightarrow R{\cdot}CO{\cdot}NBz{\cdot}NH{\cdot}CO{\cdot}R,$$

and also by the formation of benzoylhydrazobenzene, $NPhBz{\cdot}NHPh$, by heating azobenzene with benzaldehyde for fifteen hours at 110°.

The decomposition of the azodiacyls by heat has not yet been thoroughly investigated, but with azodibenzoyl and azodi-α-naphthoyl the decomposition occurs to a small extent as follows:

$$COR{\cdot}N{:}N{\cdot}CO{\cdot}R \longrightarrow COR{\cdot}COR + N_2.$$

Azodicarboxylimide and several of its derivatives of the formula (I) below (where $R = H$, Ph, NH_2, $N{:}CHPh$) have also been prepared by the action of iodine in ethereal solution on the silver salts of the corresponding hydrazo-compounds (II); they are decomposed by water as follows:

$$\underset{\text{(I.)}}{\begin{matrix} N{\cdot}CO \\ \| \\ N{\cdot}CO \end{matrix}\!\!>\!NR} + 2H_2O = \underset{\text{(II.)}}{\begin{matrix} NH{\cdot}CO \\ | \\ NH{\cdot}CO \end{matrix}\!\!>\!NR} + N_2 + 2CO_2 + R{\cdot}NH_2.$$

The *mercury* salt of *s*-dibenzoylhydrazide, $CPh\!\lessdot\!\begin{matrix} N\text{——}N \\ O{\cdot}Hg{\cdot}O \end{matrix}\!\gtrdot\!CPh$, obtained by the action of mercuric chloride on the hydrazide and sodium ethoxide in alcoholic solution, is converted by bromine in ethereal solution into azodibenzoyl (Stollé and Benrath, Abstr., 1900, i, 531; 1904, i, 935). When heated at 270° in an atmosphere of carbon dioxide, this decomposes, yielding small quantities of benzil and 2 : 5-diphenyl-1 : 3 : 4-oxadiazole. It combines with benzaldehyde at 110° to form tribenzoylhydrazide, a small amount of the above-

mentioned oxadiazole being produced simultaneously. It reacts with aniline, yielding benzanilide and *s*-dibenzoylhydrazide, thus:

$$(1)\ NBz{:}NBz + NH_2Ph = NHPhBz + N_2 + 2H$$
$$(2)\ 2H + NBz{:}NBz = NHBz{\cdot}NHBz,$$

and with dimethylaniline to form *s*-dibenzoylhydrazide, the dimethylaniline being oxidised to tetramethyldiphenylmethane and other products not yet investigated.

s-*Di*-p-*chlorobenzoylhydrazide*, prepared from hydrazine sulphate, *p*-chlorobenzoyl chloride, and aqueous sodium hydroxide, crystallises in felted needles, m. p. 289°, and reacts with sodium hydroxide in aqueous alcoholic solution to form the *sodium* salt,

$$C_6H_4Cl{\cdot}C(ONa){:}N{\cdot}NH{\cdot}CO{\cdot}C_6H_4Cl,$$

which crystallises in lustrous, pale yellow leaflets, and is oxidised by iodine in ethereal solution to *azodi*-p-*chlorobenzoyl*, $N_2(CO{\cdot}C_6H_4Cl)_2$, yellow needles, m. p. 147° (decomp.).

s-*Di-a-naphthoylhydrazide*, prepared in a similar manner, has m. p. 260°, and forms a *silver* salt, $C_{10}H_7{\cdot}C(OAg){:}N{\cdot}NH{\cdot}CO{\cdot}C_{10}H_7$, which is oxidised to *azodi-a-naphthoyl*, $N_2(CO{\cdot}C_{10}H_7)_2$. This crystallises in orange-red needles, m. p. 148°, and when heated at 140—150° loses nitrogen, yielding *di-a-naphthyldiketone*, $C_{10}H_7{\cdot}CO{\cdot}CO{\cdot}C_{10}H_7$, m. p. 187°; it reacts with water to form *a*-naphthoic acid, *s*-di-*a*-naphthoylhydrazide, and *tri-a-naphthoylhydrazide*, $C_{10}H_7{\cdot}CO{\cdot}NH{\cdot}N(CO{\cdot}C_{10}H_7)_2$, which has m. p. 188°, and has also been prepared by the action of *a*-naphthoyl chloride on the silver salt of *s*-di-*a*-naphthoylhydrazide.

The *sodium* salt of *s*-benzoylacetylhydrazide, $C_9H_9O_2N_2Na$, is converted by mercuric chloride in alcoholic solution into the *mercury* salt, $C_9H_8O_2N_2Hg$.

Benzoylazoacetyl, $NAc{:}NBz$, obtained in an impure condition as a red oil by the interaction of iodine and the preceding mercury salt in ethereal solution, is decomposed by water, yielding benzoic acid, *s*-dibenzoylhydrazide, and *dibenzoylacetylhydrazide*, $NAcBz{\cdot}NHBz$, m. p. 171°.

2-*Phenyl-5-methyl*-1 : 3 : 4-*oxadiazole*, $CMe{<}{}^{N\cdot N}_{-O-}{>}CPh$, prepared by heating *s*-benzoylacetylhydrazide with phosphoryl chloride, crystallises in lustrous plates, m. p. 67°; it forms with silver nitrate an additive *compound* crystallising in lustrous needles, m. p. 185°; an additive *compound* with mercuric chloride is also described.

Dibenzoyldiacetylhydrazide, $NAcBz{\cdot}NAcBz$, prepared either from acetyl chloride and the mercury salt of *s*-dibenzoylhydrazide or from benzoyl chloride and the mercury salt of *s*-diacetylhydrazide, crystallises in leaflets, m. p. 109°.

s-Diformylhydrazide yields a crystalline *silver* salt, $C_2H_2O_2N_2Ag_2$, which explodes when heated, and a *mercury* salt,

$$CH{<}{}^{N\text{——}N}_{O\cdot Hg\cdot O}{>}CH.$$

Azodiformyl, $N_2(CHO)_2$, prepared from the preceding mercury salt, could not be isolated on account of its instability; its ethereal solutions have a raspberry-red co our.

The *mercury* salt of *s*-diacetylhydrazide, $C_4H_6O_2N_2Hg$, prepared from

the hydrazide, sodium ethoxide, and aqueous mercuric chloride, reacts with iodine in ethereal solution in the presence of magnesium or barium oxides, yielding *azodiacetyl*, NAc:NAc, in an impure condition as a dark red oil.

s-Di-a-ethylbutyrylhydrazide, $N_2H_2(CO\cdot CHEt_2)_2$, prepared from the corresponding acid chloride and hydrazine hydrate in the presence of sodium carbonate, crystallises in white needles, m. p. 230°.

Azodi-a-ethylbutyryl, $N_2(CO\cdot CHEt_2)_2$, obtained from the *mercury* salt, $C_{12}H_{22}O_2N_2Hg$, of the preceding compound as a red oil, is decomposed by water into α-ethylbutyric acid and *tri-α-ethylbutyrylhydrazide*, $CHEt_2\cdot CO\cdot NH\cdot N(CO\cdot CHEt_2)_2$, which crystallises in colourless prisms, m. p. 95°, and has also been prepared by the interaction of α-ethylbutyryl chloride and *s*-α-diethylbutyrylhydrazide in pyridine solution at 100°. It combines with benzaldehyde, yielding *benzoyldi-α-ethylbutyrylhydrazide*, $CHEt_2\cdot CO\cdot NBz\cdot NH\cdot CO\cdot CHEt_2$, crystallising in small prisms, m. p. 123°. The latter compound may also be prepared from benzoyl chloride and *s*-di-α-ethylbutyrylhydrazide in pyridine solution.

Azodicarboxylimide [*diketodihydro*-1 : 3 : 4-*triazole*], $\begin{matrix}N\cdot CO\\ \| \quad\\ N\cdot CO\end{matrix}\!\!>NH$, obtained as a violet oil by the action of ethereal iodine on the silver salt of hydrazodicarboxylimide in the presence of barium and magnesium oxides, is instantly decomposed by water, yielding nitrogen, carbon dioxide, and hydrazodicarboxylimide.

Hydrazodicarboxylphenylimide yields the *silver* salts, $C_8H_6O_2N_3Ag$ and $C_8H_3O_2N_3Ag_2$, of which the latter is converted in the usual manner into azodicarboxylphenylimide. This forms carmine-red crystals (compare Thiele and Stange, Abstr., 1895, i, 251), gives violet solutions in ether, and decomposes when heated into phenylcarbimide and *hydrazotetracarboxyldiphenyldi-imide*, $NPh\!<\!\begin{matrix}CO\cdot N\cdot CO\\ | \\ CO\cdot N\cdot CO\end{matrix}\!>\!NPh$, which crystallises from glacial acetic acid in lustrous, white leaflets, subliming in needles without melting.

Azodicarboxylaminoimide (*azodicarboxylhydrazide*) [1-*amino*-2 : 5-*diketodihydro*-1 : 3 : 4-*triazole*], $\begin{matrix}N\cdot CO\\ \| \quad\\ N\cdot CO\end{matrix}\!\!>N\cdot NH_2$, prepared from the *silver* salt of aminourazole (Curtius and Heidenreich, Abstr., 1896, i, 143), $C_2H_2O_2N_4Ag_2$, is an unstable, violet powder; it explodes at 72°, and is slowly converted by water into aminourazole.

Azodicarboxylbenzylidenehydrazide, $\begin{matrix}N\cdot CO\\ \| \quad\\ N\cdot CO\end{matrix}\!\!>N\cdot N:CHPh$, obtained from the *silver* salt of benzylideneaminourazole (hydrazodicarboxylbenzylidenehydrazide), $C_9H_6O_2N_4Ag_2$, forms carmine-red crystals, which become colourless when heated (at 135—138°), owing to loss of nitrogen and conversion into *hydrazotetracarboxyldibenzylidenedihydrazide*, $CHPh:N\cdot N\!<\!\begin{matrix}CO\cdot N\cdot CO\\ | \\ CO\cdot N\cdot CO\end{matrix}\!>\!N\cdot N:CHPh$, m. p. 285°.

The *mercury* salts of ethyl hydrazodicarboxylate yields, with iodine in ethereal solution, ethyl azodicarboxylate (Curtius and Heidenreich,

loc. cit.), and, when heated with benzoyl chloride in carbon tetrachloride solution at 100°, forms *ethyl dibenzoylhydrazodicarboxylate*, $C_{20}H_{20}O_6N_2$, which forms white crystals, m. p. 83°. F. B.

Enzymic Decomposition of Hydrogen Peroxide. II. PERCY WAENTIG and OTTO STECHE (*Zeitsch. physiol. Chem.*, 1912, **76**, 177—213. Compare Abstr., 1911, i, 759).—The behaviour of both animal and vegetable extracts in decomposing hydrogen peroxide is very similar, and in far closer agreement with Senter's hæmase than is generally stated. This is illustrated particularly by the influence of hydrogen and hydroxyl ions on the rate of reaction—any shift in equilibrium from that prevailing in distilled water, free from carbon dioxide, causes a retardation. The reaction is, however, less sensitive when relatively large amounts of impurity are present in the extracts; this may be due to the amphoteric character of the proteins in retaining acids or bases, or to a definite protective action of the impurities analogous to that of the so-called "protective colloids." This insensitive character is specially marked in catalase solutions prepared from the alcohol precipitate of an aqueous extract of germinating barley.

The enzyme extracts behave similarly at 0° and at 30°; at the higher temperature the hydrogen ion has less, the hydroxyl ion more, influence on the rate of change. The influence of temperature on the rate is very small. The course of change does not quite correspond with the simple mass-action law; the value of K falls off even in very dilute hydrogen peroxide solutions at 0°. Dialysis yields weaker extracts, but with these a more constant value of K is obtained. The amount of enzyme is roughly proportional to the rate of change.

Exposure to ultra-violet light weakens the enzyme activity; the effect is greater in alkaline than in neutral or acid solution.

Complete precipitation of the enzyme from extracts of liver, fat, barley, etc., requires an alcohol concentration of 55%. Animal extracts show a decline in activity when the concentration of hydrogen peroxide exceeds a certain point; this is not the case with plant extracts.

It would appear that the active substance which brings about the decomposition of hydrogen peroxide is the same irrespective of origin.

E. F. A.

Preparation of Mercury *p*-Aminophenylarsinates. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 237787).—*Mercury hydrogen* p-*aminophenylarsinate*, $[NH_2\cdot C_6H_4\cdot AsO(OH)\cdot O]_2Hg$, a colourless powder, sparingly soluble in water, is prepared by stirring together an aqueous paste of *p*-aminophenylarsinic acid (2 mols.) and mercuric oxide (1 mol.). The *basic* salt, $NH_2\cdot C_6H_4\cdot AsO(OH)\cdot O\cdot Hg\cdot OH$, is obtained when equimolecular proportions of the amino-acid and mercuric chloride in the presence of alkali (2 mols.) are employed.

F. M. G. M.

Organic Chemistry.

The Autoxidation of Organic Compounds. HERMANN STAUDINGER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 216—219).—The autoxidation of compounds containing a double linking involves the formation of two oxides, one of which is symmetrical, as in the case of diphenylethylene, $\begin{array}{l}CPh_2\cdot O\\ \ \,| \qquad\ \ |\\ CH_2{-}{-}O\end{array}$, and the other unsymmetrical, as with trichloroethylene, $\begin{array}{l}CCl_3{-}\\ \ \,|\\ CHCl\end{array}\!\!>\!O\!:\!O$, which then breaks up into $\begin{array}{l}CCl_2{-}\\ \ \,|\\ CHCl\end{array}\!\!>\!O$ and oxygen. It is assumed that the first product is always the unsymmetrical compound, which may then undergo rearrangement. C. H. D.

Action of the Grignard Reagent on Methylethylacraldehyde and the Preparation of Some Diolefines, Olefines, and Saturated Secondary Alcohols. E. BJELOUSS (*Ber.*, 1912, 45, 625—632. Compare Abstr., 1910, i, 706).—*δ-Methyl-Δ^{γ}-octen-ε-ol*, $CH_2Me\cdot CH\!:\!CMe\cdot CH(OH)\cdot CH_2\cdot CH_2Me$, prepared from propyl chloride and methylethylacraldehyde, is a colourless, mobile, strongly smelling liquid, m. p. 79—81°/10 mm., D_4^{25} 0·8468, n_D 1·4445. The *acetate* is a colourless, mobile liquid, b. p. 87—89°/14 mm.; the *chloride* has b. p. 59—62°/11 mm.

γ-Methyl-$\Delta^{\alpha\gamma}$-hexadiene, $CH_2Me\cdot CH\!:\!CMe\cdot CH\!:\!CH_2$, is a very mobile, colourless liquid, b. p. 101—103°, D_4^{25} 0·7407, n_D^{25} 1·452.

δ-Methyl-$\Delta^{\gamma\epsilon}$-octadiene, $CH_2Me\cdot CH\!:\!CMe\cdot CH\!:\!CH\cdot CH_2Me$, is a colourless liquid of characteristic odour, b. p. 148—151°, D_4^{25} 0·764, n_D^{25} 1·4628.

γ-Methylhexan-β-ol, $CH_2Me\cdot CH_2\cdot CHMe\cdot CHMe\cdot OH$, is a colourless, mobile liquid with an odour of peppermint, b. p. 79—81°/52 mm., D_4^{25} 0·822, n_4^{25} 1·4207; the *acetate* is a pleasant smelling liquid, b. p. 84—87°; the *chloride* has b. p. 53—58°/36 mm.

δ-Methylheptan-γ-ol, $CH_2Me\cdot CH_2\cdot CHMe\cdot CH(OH)\cdot CH_2Me$, is an agreeable smelling liquid, b. p. 98—99°/75 mm., D_4^{25} 0·8268, n_D^{25} 1·4261; the *acetate* has b. p. 103—104°/75 mm.; the *chloride*, b. p. 83—86°/79 mm.

δ-Methyloctan-ε-ol is a colourless, strongly smelling liquid, b. p. 74—76°/9 mm., D_4^{25} 0·8156, n_D^{25} 1·4262.

βε-Dimethyloctan-δ-ol, $CH_2Me\cdot CH_2\cdot CHMe\cdot CH(OH)\cdot CH_2\cdot CHMe_2$, is similarly a colourless, mobile liquid, b. p. 102—104°/34 mm., D_4^{25} 0·8125, n_D^{25} 1·4259; the *phenylurethane* crystallises in bunches of needles, m. p. 39—40°.

βζ-Dimethylnonan-ε-ol has b. p. 98—99°/11 mm., D_4^{25} 0·8126, n_D^{25} 1·4295; the crystalline *phenylurethane* has m. p. 43—44°.

γ-Methyl-Δ^{β}-hexene, $CH_2Me\cdot CH_2\cdot CMe\!:\!CHMe$, prepared by elimination of hydrogen bromide from methylhexanyl bromide, is an exceed-

ingly volatile liquid of pleasant odour, b. p. 85—90°, D_4^{25} 0·7301, n_D^{25} 1·4132.

δ-Methyl-Δ^γ-heptene is very similar; it has b. p. 115—120°, D_4^{25} 0·7411, n_D^{25} 1·4171.

δ-Methyl-Δ^δ-octene has a penetrating odour, b. p. 133—138°, D_4^{25} 0·7388, n_4^{25} 1·4178.

βε-Dimethyl-Δ^δ-octene has b. p. 152—157°, D_4^{25} 0·746, n_D^{25} 1·4189.

δθ-Dimethyl-Δ^δ-nonene has b. p. 165—169°, D_4^{25} 0·753, n_D^{25} 1·4278.

By the action of magnesium phenyl bromide on methylethylacraldehyde an alcohol is at first formed, but on distillation in a vacuum water is eliminated and a hydrocarbon, *α-phenyl-β-methyl-Δ^αγ-pentadiene* (?), obtained; this is a yellow, mobile, strong smelling liquid, b. p. 228—231°/753 mm., D_4^{25} 0·8986, n_D^{25} 1·5257.

α-Phenyl-β-methylpentane, obtained on reducing phenylmethylpentenol, is a colourless, mobile, pleasant smelling liquid, b. p. 203—207°, D_4^{25} 0·8584, n_D^{25} 1·4827.

α-Naphthyl-β-methyl-Δ^αγ-pentadiene (?) is a yellow liquid of characteristic odour, b. p. 178—181°/12 mm., D_4^{25} 0·9801, n_D^{25} 1·5697.

E. F. A.

Compounds with Triple Linkings. WILHELM MANCHOT [with JOHN C. WITHERS and HEINRICH OLTROGGE] (*Annalen*, 1912, **387**, 257—293).—Various observers have described additive compounds of acetylene and cuprous chloride, but have been unable to show that their substances are initial products of the reaction. The authors, using a modified form of the apparatus described previously (Abstr., 1910, i, 85), now show that the initial product is the white *substance*, $C_2H_2,CuCl$. On account of its solubility and of the secondary reaction which occurs in concentrated solutions, this substance cannot be isolated from aqueous solutions; it is obtained, however, by working in absolute alcoholic solution at 0°. At 0° and atmospheric pressure, experiments with solutions containing 0·034 gram-molecule of cuprous chloride per litre and varying quantities of hydrochloric acid yield the following results. With 0·61 gram-molecule of hydrochloric acid per litre, a clear, colourless solution is obtained, and 22·44 litres of acetylene (per 1 gram atom of copper) are absorbed. With greater concentrations of hydrochloric acid, the absorption of acetylene diminishes owing to the concurrent reaction: $CuCl + HCl = CuCl,HCl$. When the concentration of the hydrochloric acid is less than 0·61 mol. per litre, the absorption of acetylene also diminishes, owing to the formation of a dark violet *substance*, $C_2Cu_2,CuCl,H_2O$.

When the concentration of the cuprous chloride in a solution of 0·61 mol. of hydrochloric acid per litre is increased, the absorption of acetylene diminishes, owing to the formation of a sparingly soluble white *substance*, $2CuCl,C_2H_2$; thus: $2(CuCl,C_2H_2) \rightleftarrows C_2H_2 + 2CuCl,C_2H_2$. For example, the absorption of acetylene is 22·4 litres (per 1 gram atom of copper) when the concentration of the cuprous chloride is 0·00561 mol. of cuprous chloride, and only 11·43 litres when the concentration is increased to 0·5035 mol.

In its ability to form a compound of the type $2CuCl,C_2H_2$, acetylene differs from carbon monoxide and ethylene, and resembles nitric oxide

which can form a compound $2FeSO_4,NO$ (Abstr., 1907, ii, 93; 1908, ii, 375; 1910, i, 85; ii, 414, 956). The additive capacity of acetylene towards cuprous chloride also differs from those of carbon monoxide and ethylene in the following respect. The latter two gases only form additive compounds in the presence of water, ammonia, or organic bases; the presence of alcohol not only retards the addition, but causes decomposition of the additive compound when formed. In the case of acetylene the presence of water is unnecessary for the formation of the additive compound $CuCl,C_2H_2$; the additive compound is formed, as in the case of nitric oxide and ferrous chloride, in absolute alcohol.

Substituted acetylenes, such as phenylacetylene, *p*-anisylacetylene, methylenedioxyphenylacetylene, behave like acetylene itself towards cuprous chloride. By direct addition of the components, colourless additive compounds of the type CR⋮CH,CuCl are obtained, which are converted by water or ammonia into coloured copper derivatives, CR⋮CCu. Hence the equation CR⋮CH + CuCl = CR⋮CCu + HCl expresses only the initial and the final states; the first phase of the process, that is, the condition for the subsequent substitution, is the formation of an additive compound of the two components. These experiments, therefore, support the views on processes of substitution recently advanced by Werner and by E. Fischer.

The presence of the group ⋮CH is not the condition for the formation of additive compounds of acetylenes and metallic salts, because, although many substances of the type CR⋮CR′ do not form additive compounds, bromophenylacetylene, iodophenylacetylene, phenylpropiolonitrile, and phenylpropiolamide react readily with cuprous chloride to form such substances.

The authors are of opinion that the degree of unsaturation of substances containing a triple linking varies from case to case with the nature of the groups attached to the C⋮C group. Even if a group R is itself unsaturated, it does not necessarily increase the unsaturation of the whole molecule CR⋮CR′; thus, diphenyldiacetylene, di-*p*-anisyldiacetylene, and bis-3 : 4-methylenedioxyphenyldiacetylene do not form additive compounds with cuprous chloride.

The following new compounds are described: *p*-Anisylacetylene forms a canary-yellow *copper* derivative, $OMe{\cdot}C_6H_4{\cdot}C{⋮}CCu$, and a colourless additive *compound*, $OMe{\cdot}C_6H_4{\cdot}C{⋮}CH,CuCl$, and yields by treatment in ether with sodium and subsequently with benzoyl chloride, *benzoyl-*p*-anisylacetylene*, $OMe{\cdot}C_6H_4{\cdot}C{⋮}CBz$, m. p. 81°, which does not react with cuprous chloride and forms a *dibromide*, $OMe{\cdot}C_6H_4{\cdot}CBr{\cdot}CBrBz$, m. p. 90°. *Di-*p*-anisyldiacetylene*,

$$C_2(C{\cdot}C_6H_4{\cdot}OMe)_2,$$

m. p. 144°, white needles, is obtained almost quantitatively by shaking the copper derivative of *p*-anisylacetylene with alcoholic ammonia and oxygen for four days. *Bis-3 : 4-methylenedioxyphenyldiacetylene*, $C_{18}H_{10}O_4$, m. p. 197°, and diphenyldiacetylene are prepared in a similar manner.

C. S.

Derivatives of Acetylene. HUGO NOERDLINGER (*Kleine Mitt. Chem. Fabrik. Flörsheim*, No. 37).—The physical constants and properties of the following derivatives of acetylene are given: Heptinene (*n*-amyl-

acetylene, b. p. 108—110°/745 mm., 26°/10 mm., m. p. below −70°, D^{15} 0·7546, D^{20} 0·7470. Octinene (*n*-hexylacetylene), b. p. 130—132°/745 mm., 31°/8 mm., m. p. below −70°, D^{15} 0·7680. *Noninene* (n-*heptylacetylene*), b. p. 160°/745 mm., 51°/8 mm., m. p. −65°, D^{15} 0·7799. *Decinene* (n-*octylacetylene*), b. p. 181—182°/745 mm., 69—70°/10 mm., m. p. −36°, D^{15} 0·7924. *Undecinene* (n-*nonylacetylene*), b. p. 202—204°/745 mm., 91°/8 mm., m. p. −33°, D^{15} 0·8024.

All these compounds are colourless liquids, practically insoluble in water, soluble in organic solvents. They possess a high refractive index, and a characteristic odour which is particularly marked in the cases of heptinene and undecinene. With ammoniacal cuprous chloride and silver nitrate solutions, they yield yellow and white precipitates respectively. When dissolved in ether and treated with sodium, they evolve hydrogen and form highly reactive sodium compounds. H. W.

Density and Thermal Expansion of Ethyl Alcohol and its Mixtures with Water. N. S. OSBORNE, E. C. MCKELVY, and H. W. BEARCE (*J. Washington Acad. Sci.*, 1912, 2, 95—98).—The densities of twelve mixtures of ethyl alcohol and water were determined at 10°, 15°, 20°, 25°, 30°, 35°, and 40° by the method of hydrostatic weighing. For each mixture the constants α, β, and γ in the equation $D_{t°} = D_{25°} + \alpha(t - 25°) + \beta(t - 25°)^2 + \gamma(t - 25°)^3$, and these values are tabulated together with $D^{25°}$.

The values of α, β, and γ for each integral % of alcohol between 0 and 100 have been obtained by interpolation. The mean of fifteen determinations of the density of the purest alcohol at 25° was found to be 0·78506. H. M. D.

Action of the Chlorides of α-Alkyloxy-acids on Organometallic Derivatives of Zinc. EDMOND E. BLAISE and L. PICARD (*Ann. Chim. Phys.*, 1912, [viii], 25, 253—276).—For the most part a résumé of work already published (Abstr., 1911, i, 175, 260). The following new data are recorded regarding substances obtained in the general reaction.

Ethyl n-*amyl ether*, b. p. 119—120°, is a mobile, pleasant smelling liquid, insoluble in water, which on heating with hydriodic acid yields *n*-amyl iodide, from which *n*-amyl ether, b. p. 70°/12 mm., and *n*-amyl alcohol were prepared. The *phenylurethane* of the latter has m. p. 46°, and crystallises in tablets, and the *benzoate* boils at 137—138°/15 mm. *Ethoxymethyl* n-*butyl ketone*, $OEt\cdot CH_2\cdot CO\cdot C_4H_9$, b. p. 79°/18 mm., is a pleasant-smelling liquid; the *oxime*, b. p. 125°/17 mm., is a colourless liquid; the *semicarbazone*, m. p. 99°, forms brilliant, colourless spangles.

Condensation of ethoxyacetyl chloride with zinc *iso*amyl iodide furnished *ethyl* iso*hexyl ether*, $OEt\cdot CH_2\cdot CH_2Pr^{\beta}$, b. p. 68°/67 mm., or 137°/760 mm., and ethoxymethylhexanone (Sommelet, Abstr., 1907, i, 107).

p-*Tolylethoxymethylethylcarbinol*, $OH\cdot CEt(CH_2\cdot OEt)\cdot C_6H_4Me$, b. p. 130°/9 mm., obtained by the action of magnesium ethyl bromide on

p-tolylethoxymethyl ketone already described (Abstr., 1911, i, 175), gives by the application of Sommelet's method (*loc. cit.*), *β*-p-*tolylbutaldehyde*, $C_6H_4Me\cdot CHEt\cdot CHO$, b. p. 104°/8 mm. The latter furnishes an *azine*, m. p. 63° (decomp.), a *semicarbazone*, p-*nitrophenylhydrazone*, m. p. 104°, and an *oxime*, m. p. 70°, all of which are crystalline. T. A. H.

Action of Alkyloxides on Esters of Inorganic Acids. I. L. RABTSEVITSCH-ZUBKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 44, 151—154).—Methyl sulphate reacts with magnesium methoxide according to the equation: $2Me_2SO_4 + Mg(OMe)_2 = 2Me_2O + Mg(SO_4Me)_2$, and with sodium *iso*butoxide according to:

$$Me_2SO_4 + CHMe_2\cdot CH_2\cdot ONa = NaMeSO_4 + CHMe_2\cdot CH_2\cdot OMe.$$

Magnesium methoxide and methyl phosphate yield methyl ether, and magnesium dimethyl phosphate: $PO(OMe)_3 + Mg(OMe)_2 = 2Me_2O + Mg[O\cdot PO(OMe)_2]_2$; so that when alkyloxides react with alkyl salts of polybasic inorganic acids, only one of the alkyloxy-groups of the salt is replaced by the metal of the alkyloxide. T. H. P.

Preparation of Aminoethyl Alcohol from Egg Lecithin. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, 76, 496—498. Compare Abstr., 1911, i, 771).—*β*-Aminoethyl alcohol is obtained as a product of the hydrolysis of egg lecithin by dilute sulphuric acid in not inconsiderable quantity, and identified by means of the aurichloride. E. F. A.

Should the Term Protagon be Retained? WALDEMAR KOCH (*Proc. Amer. Soc. Biol. Chem.*, 1911, xl; *J. Biol. Chem.*, 11).—The term protagon has no longer any chemical significance; the substance so described contains at least three materials, namely, a phosphatide, which contains choline, a cerebroside, and a combination of a choline-free phosphatide and a cerebroside to which an ethereal sulphuric acid group is attached. W. D. H.

New Compounds of Samarium and Neodymium. CHARLES JAMES, F. M. HOBEN, and C. H. ROBINSON (*J. Amer. Chem. Soc.*, 1912, 34, 276—281; *Chem. News*, 1912, 105, 121—122).—In the course of a search for salts which might be of value for fractionally separating the rare earths, the following compounds were prepared and are described.

Samarium ethylsulphonate, $(C_2H_5\cdot SO_3)_6Sa_2,6H_2O$, *methylsulphonate*, $(CH_3\cdot SO_3)_6Sa_2,7H_2O$, *propylsulphonate*, $(C_3H_7\cdot SO_3)_6Sa_2,9H_2O$, iso*butylsulphonate*, $(C_4H_9\cdot SO_3)_6Sa_2,7H_2O$, *camphorsulphonate*,

$$(C_{10}H_{15}O\cdot SO_3)_6Sa_2,10H_2O,$$

methanetrisulphonate, $[CH(SO_3)_3]_2Sa_2,16H_2O$, m-*xylene-4-sulphonate*, $(C_6H_3Me_2\cdot SO_3)_6Sa_2,7H_2O$, *glycollate*, $(OH\cdot CH_2\cdot CO_2)_6Sa_2$, *cacodylate*, $(Me_2AsO_2)_6Sa_2,16H_2O$, *ethanedisulphonate*, $[C_2H_4(SO_3)_2]_3Sa_2,4H_2O$, *ethylglycollate*, $(OEt\cdot CH_2\cdot CO_2)_2Sa_2,18H_2O$, *citraconate*,

$$(C_5H_4O_4)_3,Sa_2,12H_2O,$$

sulphoacetate, $(C_2H_2O_5S)_3Sa_2$, and *hydroxyethanesulphonate*. *Neodymium methylsulphonate*, $(CH_3\cdot SO_3)_6Nd_2,7H_2O$, *ethylsulphonate*,

$$(C_2H_5\cdot SO_3)_6Nd_2,6H_2O,$$

propylsulphonate, $(C_3H_7{\cdot}SO_3)_6Nd_2,6H_2O$, *isobutylsulphonate*, $(C_4H_9{\cdot}SO_3)_6Nd_2,8H_2O$, *ethanedisulphonate*, $[C_2H_4(SO_3)_2]_3Nd_2,10H_2O$, *methanetrisulphonate*, $[CH(SO_3)_3]_2Nd_2,14H_2O$, *camphorsulphonate*, $(C_{10}H_{15}O{\cdot}SO_3)_6Nd_2,17H_2O$, m-*xylene-4-sulphonate*, $(C_6H_3Me_2{\cdot}SO_3)_6Nd_2,2H_2O$, m-*sulphobenzoate*, $(C_7H_4O_5S)_3Nd_2,9H_2O$, *quinate*, $[C_6H_7(OH)_4{\cdot}CO_2]_6Nd_2,11H_2O$, *anisate*, $(OMe{\cdot}C_6H_4{\cdot}CO_2)_6Nd_2$, *oxanilate*, $(NHPh{\cdot}CO{\cdot}CO_2)_6Nd_2,5H_2O$, *cacodylate*, $(Me_2AsO_2)_6Nd_2$, and *hydroxyethanesulphonate*. E. G.

Reduction of Higher Unsaturated Aliphatic Acids to Saturated Acids by the Action of Zinc and Water on their Halogen Derivatives; Grignard Reaction Applied to the Latter. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 155—165).—Experiments with oleic, elaidic, erucic, undecenoic, ricinoleic, linoleic, and linolenic acids show that by addition of hydrogen bromide to these acids and treatment of the monobromo-saturated acids thus obtained with zinc and water in a sealed tube, the corresponding saturated aliphatic acids themselves are obtained; for example, $(C_{17}H_{34}Br{\cdot}CO_2)_2Zn + 2Zn + H_2O = (C_{17}H_{35}{\cdot}CO_2)_2Zn + (ZnBr_2 + ZnH)_2$. Unsaturated hydroxy-acids may be converted into saturated hydroxy-acids in a similar manner. With monochloro-derivatives of saturated aliphatic acids, the reaction with zinc and water proceeds partly in the direction indicated by the above equation, but about one-third of the acid formed consists of the original unsaturated acid, from which the chloro-derivative of the saturated acid was obtained. As stated by Lewkowitsch ("Oils, Fats, and Waxes"), neither dichloro- nor dibromo-stearic acid gives the non-substituted stearic acid when heated with various metals in presence or absence of water or an organic solvent.

The following temperatures are those at which fused mixtures of oleic and stearic acid solidify: 10% stearic acid (90% oleic), 29·5°; 20%, 40·2°; 30%, 47·7°; 40%, 52·9°; 50%, 56·8°; 60%, 59·8°; 70%, 62·3°; 80%, 64·5°; 90%, 66·3°, and pure stearic acid, 68·0°. T. H. P.

An Anomaly in the Reduction of Ethyl Acetoacetate. JULIUS TAFEL [with FRANZ ANDRE] (*Ber.*, 1912, **45**, 437—452. Compare Tafel and Hahl, Abstr., 1907, i, 765; Tafel and Jürgens, Abstr., 1909, i, 545).—The electrolytic reduction of derivatives of acetoacetic esters has been interpreted to take place according to the scheme: $CH_3{\cdot}CO{\cdot}CHR{\cdot}CO_2Et \longrightarrow CH_3{\cdot}CH_2{\cdot}CHR{\cdot}CH_3$. Whilst, however, the range of the b. p. of the products obtained points to their uniformity, the actual b. p.'s do not in all cases agree with those recorded for the expected hydrocarbons, and in the cases where R = Et, *n*Pr, or nC_4H_9, lie close to those of the isomeric normal hydrocarbons; similarly, Tafel and Jürgens (*loc. cit.*) found for the reduction-product of ethyl *iso*butylacetoacetate a b. p. 7° higher than that given by Clarke (Abstr., 1908, i, 593) for βδ-dimethylhexane. The present work was undertaken with the object of explaining these differences,

and has led to the conclusion that the methyl group formed in the complete reduction of derivatives of acetoacetic esters is transposed and occurs, not as a side-chain, but as part of the main chain.

The reduction of ethyl *iso*butylacetoacetate, whether with lead or cadmium electrodes, gave results precisely similar to those obtained by Tafel and Jürgens (*loc. cit.*) The product, which is now regarded as β-methylheptane or γ-methylheptane (instead of $\beta\delta$-dimethylhexane), appears to undergo slight decomposition when shaken with concentrated sulphuric acid according to the method previously used for its purification.

By the reduction of ethyl *sec.*-butylacetoacetate with lead electrodes, a hydrocarbon, b. p. 117·8—118·2°/746 mm., was obtained. This is regarded as γ-methylheptane or, possibly, a mixture of δ-methylheptane and γ-ethylhexane.

Methyl methylpropylacetoacetate, reduced at a cadmium electrode, yielded an octane of b. p. 116·1—118·2°/752 mm. This is probably δ-methylheptane, possibly γ-methylheptane or γ-ethylhexane, or a mixture of the latter with δ-methylheptane.

Methyl methyl*iso*propylacetoacetate when similarly reduced gave an octane of b. p. 110—118°/756 mm., which is presumably a mixture of hydrocarbons.

By the reduction of ethyl *iso*propylacetoacetate, a heptane of b. p. 91—92·6°/747 mm., probably slightly impure β-methylhexane, or possibly γ-methylhexane, was obtained.

Ethyl ethylacetoacetate when reduced at cadmium or lead electrodes yielded a hydrocarbon which, after purification by means of concentrated sulphuric acid, had b. p. 68·2—69·1°/742 mm. This was unaffected by cold potassium permanganate, thereby differing from γ-methylheptane, which, according to Zelinsky and Zelikoff, is rapidly oxidised by this reagent—a statement, however, which the authors could not confirm experimentally.

An explanation of certain of these reactions may be found in the hypothesis that a tetramethylene ring is formed as an intermediate step in the reduction, and then broken in the manner indicated by the scheme:

$$\begin{array}{l} 4\ \mathrm{CH_3} \\ 3\ \mathrm{CO} \\ 2\ \mathrm{CHR} \\ 1\ \mathrm{CO_2Et} \end{array} \longrightarrow \begin{array}{cc} 4 & 3 \\ \mathrm{C}- & \mathrm{C} \\ | & | \\ \mathrm{C}- & \mathrm{C}-\mathrm{R} \\ 1 & 2 \end{array} \longrightarrow \begin{array}{l} 1\ \mathrm{CH_3} \\ 4\ \mathrm{CH_2} \\ 3\ \mathrm{CH_2} \\ 2\ \mathrm{CH_2R} \end{array}$$

To explain the formation of γ-methyl derivatives from ethyl *iso*-butyl- and *iso*propyl-acetoacetates, it is necessary to assume that the carbon atom of the carbethoxy-group of the ester becomes detached from the α-carbon atom (*) and attached to a terminal C-atom of the alkyl group:

$$\begin{array}{l} \mathrm{CH_3\cdot CO\cdot \overset{*}{C}H - CH\cdot CH_3} \\ \qquad\quad \mathrm{CO_2Et\ CH_3} \end{array} \longrightarrow \begin{array}{l} \mathrm{CH_3\cdot CH_2\cdot \overset{*}{C}H_2\cdot CH\cdot CH_2\cdot CH_3} \\ \qquad\qquad\qquad\quad \mathrm{CH_3} \end{array}$$

This leads to the same result as the above hypothesis in the cases of *n*-alkyl derivatives of ethyl acetoacetate and of ethyl diethylaceto-

acetate. In the cases of *sec.*-butyl, methylpropyl, and methyl*iso*propyl derivatives, however, two products might be expected, whilst only one has been obtained, possibly owing to the proximity of their respective b. p.'s. On the whole, the second hypothesis explains the fact better than the first, but is advanced with caution on account of the difficulty of interpreting the mechanism involved.

A third possibility lies in the assumption of a new formulation for the substitution products of ethyl acetoacetate as shown in the following scheme:

$$\begin{array}{ccc} CH_3\cdot CO & CH_3\cdot CO & CH_3\cdot CO \\ | & | & | \\ CH & CH & CR_1 \\ |\!>\!O & |\!>\!O & |\!>\!O \\ H\cdot C\cdot OEt & R\cdot C\cdot OEt & R\cdot C\cdot OEt \end{array}$$

Possibly in ethyl acetoacetate this form may be in equilibrium with the forms generally assumed, and may also be the form mainly attacked during alkylation. According to this hypothesis, the same hydrocarbons should be obtained from monoalkyl derivatives of ethyl acetoacetate and from ethyl diethylacetoacetate as would be expected from the first hypothesis (see above). Ethyl methylpropylacetoacetate (from ethyl methylacetoacetate) should yield γ-ethylhexane, whilst ethyl methyl*iso*propylacetoacetate (from ethyl methylacetoacetate) and ethyl methylbenzylacetoacetate (from ethyl benzylacetoacetate) should yield β-methyl-γ-ethylpentane and α-phenyl-γ-methylpentane respectively. H. W.

A New Salt of β-Hydroxybutyric Acid. PHILLIP A. SHAFFER (*Proc. Amer. Soc. Biol. Chem.*, 1911, xi; *J. Biol. Chem.*, 11).—If equivalent parts of zinc and calcium β-hydroxybutyrates (made by treating the free acid with zinc and calcium carbonate respectively) are poured together, a double salt, $ZnCa(C_4H_7O_3)_4$, is formed, which on the addition to the warmed solution of an equal volume of alcohol, crystallises out in needles or long, narrow plates. It is useful for the purification of the acid, which may be obtained from the double salt by removing the zinc with hydrogen sulphide, and the calcium with oxalic acid; or a solution of the salt acidified with sulphuric acid and dehydrated by plaster or anhydrous sodium sulphate may be extracted with dry ether. The salt prepared from the *l*-acid has a specific rotation, $[\alpha]_D^{20} = -15{\cdot}1°$ (5% solution). W. D. H.

Syntheses by means of Mixed Organo-metallic Derivatives. Mixed *cyclo*Acetals. EDMOND É. BLAISE (*Compt. rend.*, 1912, **154**, 596—598. Compare Abstr., 1911, i, 175, 260).—The action of organo-zinc halides on acid chlorides of the type $COCl\cdot CHR\cdot O\cdot CO\cdot R$ is abnormal, and leads to the production of cyclic compounds which the author proposes to term *cyclo*acetals. An intermediate compound is probably decomposed in the following manner:

$$ZnI\cdot O\cdot CR_2\cdot O\cdot CHR\cdot COCl = ZnICl + CHR{<}\begin{matrix}CO\cdot O\\ O\end{matrix}{>}CR_2.$$

The following new substances have been prepared; their use in the

synthesis of aldehydes, α-ketonic acids, and α-halogen ketones will be described in a subsequent communication.

$$CHMe<\substack{CO\cdot O\\ O}>CMePr^{\alpha}, \text{ b. p. } 90°/22 \text{ mm.}$$

$$CMe_2<\substack{CO\cdot O\\ O}>CMeEt, \text{ b. p. } 64°/13 \text{ mm.}$$

$$CH_2Me\cdot[CH_2]_2\cdot CH<\substack{CO\cdot O\\ O}>CMeEt, \text{ b. p. } 103°/12 \text{ mm.}$$

$$CH_2Me\cdot[CH_2]_3\cdot CH<\substack{CO\cdot O\\ O}>CMeEt, \text{ b. p. } 115°/12 \text{ mm.}$$

Acetylsalicoyl chloride gives the *compound*, $C_6H_4<\substack{CO\cdot O\\ O}>CMeEt$, whilst acetyl *p*-hydroxybenzoyl chloride behaves normally.

W. O. W.

Formation of Cork. SIMON ZEISEL (*J. pr. Chem.*, 1912, [ii], 85, 226—230).—Polemical with Schmidt (this vol., i, 72). F. B.

Oxidation Products of Sebacic Acid. EYVIND BÖDTKER (*J. pr. Chem.*, 1912, [ii], **85**, 221—225).—Succinic, glutaric, and adipic acids, together with a small quantity of γ-heptanone-$\alpha\eta$-dicarboxylic acid (Tönnies, Abstr., 1879, 915), are the only products formed when sebacic acid is boiled with concentrated nitric acid until it completely disappears. For details of the separation of the acids, the original should be consulted. F. B.

Dissociation of Tartrates, Malates, and Camphorates of Amines as Revealed by their Rotatory Power. JULES MINGUIN (*Ann. Chim. Phys.*, 1912, [viii], **25**, 145—159).—The work on tartrates has been published already, and the general conclusions then drawn apply to the other salts now dealt with (Minguin and Wohlgemuth, Abstr., 1909, i, 11). The malates and camphorates of the aliphatic amines exist undissociated in solution, but in the case of the aromatic amines neutral malates are not formed and the hydrogen malates are dissociated in solution. Camphorates of the aromatic amines do not exist in solution. The hydrogen malates of aniline and of diethylaniline melt at 132° and 67° respectively. T. A. H.

Lactonisation of α-Ketonic Esters. Ethyl Pyruvate. HENRI GAULT (*Compt. rend.*, 1912, **154**, 439—441. Compare Abstr., 1911, i, 709; de Jong, Abstr., 1904, i, 550).—When the lactonisation of ethyl pyruvate is effected by saturating the ester with hydrogen chloride in the cold, the ethyl α-keto-γ-valerolactone-γ-carboxylate first formed undergoes further change, and a neutral substance, b. p. 176—177°/13 mm., is obtained; this is probably the ethyl ether of the enolic form of the above ketone, $CO_2Et\cdot CMe<\substack{O-CO\\ CH:C\cdot OEt}$, and appears to be identical with the compound prepared by Genvresse (Abstr., 1893, i, 552), which he supposed to be ethyl α-keto-Δ^{β}-butene-$\alpha\gamma$-dicarboxylate. It unites with hydrazine (2 mols.) to form a *compound*, m. p. 180° (decomp.), the constitution of which has not yet been elucidated.

W. O. W.

Citrophosphate Solutions. ANTONIO QUARTAROLI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 130—135).—The author criticises the work of Pratolongo (Abstr., 1911, ii, 865) on this subject. The supposed solutions of diammonium citrate used by that author are shown to have contained a mixture of diammonium and triammonium citrates with an excess of the latter. The differences between the cryoscopic depressions observed by Pratolongo and the calculated values are not due to hydrolysis, because they would require, for instance, that not only the diammonium citrate, but also three-quarters of the mon-ammonium citrate present should suffer hydrolysis. The present author's calculations (from the dissociation constants of ammonium hydroxide and citric acid) show that even triammonium citrate can be but little hydrolysed. The abnormal values obtained for *i* in the case of the ammonium citrates are therefore due, not to hydrolysis, but to electrolytic dissociation. It is further shown that the cryoscopic data do, in fact, support the hypothesis of the formation of complex salts, and exclude the possibility of the occurrence of double decomposition.

The paper records cryoscopic measurements for various solutions of citric acid, monoammonium citrate, triammonium citrate (and four intermediate solutions between the two last named), monopotassium citrate, dipotassium citrate, tripotassium citrate, monoammonium phosphate, diammonium phosphate, triammonium phosphate, tri-ammonium citrate + calcium hydrogen phosphate, and triammonium citrate + barium hydrogen phosphate. R. V. S.

The Synthetic Application of Ethyl Methanetricarboxylate. ROLAND SCHOLL (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 213—214).—The usual ethyl acetoacetate and ethyl malonate syntheses may be performed with ethyl methanetricarboxylate if alcohol is excluded. The reaction takes place at or above 100°, and a pure product is obtained. *Ethyl methanetetracarboxylate*, prepared from ethyl sodiomethanetricarboxylate and ethyl chloroformate, is a stable compound, b. p. above 290° undecomposed, and yielding malonic acid with dilute sulphuric acid. C. H. D.

New Method for the Catalytic Preparation of Aldehydes from Acids. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1912, **154**, 561—564. Compare this vol., i, 156, 157).—The reduction of aliphatic acids by means of formic acid furnishes a convenient method for preparing the corresponding aldehydes with satisfactory yields. The vapour of the acid, mixed with excess of formic acid, is passed over titanium oxide at 250—300°. Under these conditions, no ketone is formed, but the formic acid decomposes into carbon monoxide and water, thus effecting reduction of the acid. The following acids readily give aldehydes, the numbers indicating the yield in percentages: acetic 50, phenylacetic 75, propionic 40, butyric 55, *iso*butyric 65, *iso*valeric 75, γ-methylvaleric 80, octoic 95, and nonoic acid 85%. In the last case, a small amount of the corresponding ketone, pelargone, is also formed. Crotonic acid gives the aldehyde.

When thoria is substituted for titanium oxide, the yields of aldehyde are lower. W. O. W.

Alfalfone, a Ketone of the Formula $C_{21}H_{42}O$, obtained from Alfalfa. Alfalfa Investigation. II. C. A. JACOBSON (*J. Amer. Chem. Soc.*, 1912, **34**, 300—302).—In an earlier paper (this vol., ii, 80) it was shown that myristone is present in alfalfa meal. Another *ketone*, $C_{21}H_{42}O$, m. p. 88·5—88·8°, has now been isolated in the form of a white, amorphous powder, and has been termed *alfalfone*. On reducing this ketone with sodium and alcohol, the corresponding *carbinol*, $C_{21}H_{43}\cdot OH$, m. p. 86·3—86·5°, is produced as a white, amorphous powder. E. G.

New Anhydrides of Dextrose and Glucosides. EMIL FISCHER and KARL ZACH (*Ber.*, 1912, **45**, 456—465).—By the action of barium hydroxide on triacetylmethylglucoside bromohydrin (Fischer and Armstrong, Abstr., 1902, i, 263), the authors have isolated a substance, $C_7H_{12}O_5$, which they provisionally name anhydromethylglucoside. It forms a crystalline *hydrate*, and is not converted into sugar by emulsin. Warm dilute acids convert it into *anhydrodextrose*, $C_6H_{10}O_5$, which strongly resembles the hexoses, differing from them, however, in its much greater ability to restore the colour to Schiff's reagent. It yields a *hydrazone* and an *osazone*.

The transformation of acetyldibromodextrose into *triacetyldextrose bromohydrin* and into *triacetylmentholglucoside bromohydrin* is also described together with the formation of *anhydromentholglucoside* from the latter substance.

Anhydromethylglucoside was prepared by warming triacetylmethylglucoside bromohydrin with barium hydroxide in aqueous alcoholic solution. After filtration and evaporation, the residue was distilled under a pressure of 0·2—0·3 mm., when the anhydride passed over between 160° and 165° (temp of bath) as a colourless syrup. In aqueous solution it had $[\alpha]_D^{23}$ $-136·95°$. Under suitable conditions it formed a hydrate which was not obtained free from syrup. At 56°/12 mm. it still retained water. When dried over phosphoric oxide at 100°/12 mm., it melted, lost all its water, and left a residue of anhydromethylglucoside.

Anhydrodextrose was formed by hydrolysing anhydromethylglucoside with 4·5% sulphuric acid. It crystallised in long needles, m. p. 118° (corr.) after slight softening. In aqueous solution it had $[\alpha]_D^{20}$ $+53·89°$. It dissolved readily in water and alcohol, with difficulty in ethyl acetate.

Anhydrodextrosephenylhydrazone was best prepared by mixing anhydrodextrose with pure phenylhydrazine. The solid mass obtained by gently warming the mixture was washed with ether and crystallised from water, from which the phenylhydrazone separated in faintly yellow leaflets, m. p. 157—158° (corr.).

Anhydrodextrosephenylosazone, prepared in the same manner as dextrosephenylosazone, crystallised in slender needles. It darkened when heated, and had m. p. about 180° (corr. decomp.).

Triacetylmenthol-*d*-glucoside bromohydrin was formed when ethereal solutions of acetyldibromodextrose and menthol were shaken with silver carbonate. It separated from alcohol in long needles, m. p. 140° (corr.), and had $[\alpha]_D^{20}$ $-49·62°$ in chloroform solution. Treat-

ment with sodium hydroxide in alcoholic solution transformed it into anhydromentholglucoside, m. p. 113° (corr.), $[\alpha]_D^{25}$ $-96{\cdot}73°$ in alcoholic solution.

Triacetylbenzylglucoside bromohydrin was obtained in the same manner as the above menthol compound. It had m. p. 141° (corr.) after previous softening, $[\alpha]_D^{20}$ $-46{\cdot}76°$ in chloroform solution.

Acetyldibromodextrose when shaken in acetone solution with silver carbonate yielded triacetyldextrose bromohydrin, m. p. 119° (corr.), $[\alpha]_D^{20}$ $+23{\cdot}33°$ in acetone solution. Mutarotation has not yet been observed with this compound. H. W.

Dextrinisation of Starch by Desiccation. GIOVANNI MALFITANO and (Mlle.) A. MOSCHKOFF (*Compt. rend.*, 1912, **154**, 443—446).—The conversion of starch into dextrin is attributed to progressive dehydration of the substance, and not to the ordinary hydrolytic action of water. Starch was dehydrated over phosphoric oxide at the ordinary temperature and at higher temperatures up to 150°, the loss of water, percentage of carbon and hydrogen, and amount of soluble matter formed being determined from time to time. In a vacuum, at 25°, 28·1% of soluble matter was formed after twenty days; this rose to 90% when the material was heated for four hours at 120°. Some decomposition occurs, even at 50°, before dehydration is complete, as is shown by the starch turning brown. This, however, is not the cause of increased solubility, for at 150° solubility is less, and analysis shows that no oxidation has occurred.

These experiments lead to the suggestion that the starch micro-cells are composed of molecules of $C_6H_{10}O_5$, linked together by water, in a manner represented by the formula

$$\{[(C_6H_{10}O_5{\cdot}OH)H](C_6H_{10}O_5{\cdot}OH)\}H \ldots,$$

or more accurately as

$$\{[(C_6H_{10}O_5{\cdot}OH)H]_n[(C_6H_{10}O_5{\cdot}OH)]_nH_{n-1}\}H \ldots$$

Soluble starch, amylodextrin, erythrodextrin, etc., may be regarded as arising by successive removals of $C_6H_{10}O_5$ groups. When dextrinisation occurs in the ordinary way by heating starch with water, the effect is the same, but the mechanism is different, water between the complexes being removed by ionisation. W. O. W.

Lintner Soluble Starch. ERNEST D. CLARK (*Biochem. Bulletin*, 1911, 1, 194—206).—A study of the reducing power and erythrodextrin reaction with iodine on Lintner soluble starch prepared from potato starch. The product can only be purified with the greatest difficulty, if at all, from the dextrin to which these reactions are due. W. D. H.

Action of Tetrabromoethane on Organic Bases. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1912, **34**, 286—290).—When tetrabromoethane is added to a solution of an organic base in dry ether, the hydrobromide of the base is precipitated and tribromoethylene is produced and remains in the solution. The reaction takes place more easily with aliphatic amines than with aromatic bases, and more easily with primary than with secondary or tertiary amines. It is

accelerated by direct sunlight. The hydrobromides of various amines have been obtained in the pure state by this method, and their mercuribromides and auribromides prepared.

When piperidine is added to an ethereal solution of tetrabromoethane, the hydrobromide is instantaneously and quantitatively precipitated, and this constitutes a convenient and inexpensive method for the preparation of tribromoethylene.

The following salts are described: *Ethylamine mercuribromide*, $NH_2Et,HBr,HgBr_2$, m. p. 91°. *Diethylamine hydrobromide*, m. p. 205°, *auribromide*, $NHEt_2,HBr,AuBr_3$, m. p. 162°, and *mercuribromide*, m. p. 120°. *Triethylamine auribromide*, m. p. 140°, and *mercuribromide*, m. p. 109°. *Dipropylamine hydrobromide*, m. p. 271°, *auribromide*, m. p. 119°, and *mercuribromide*, m. p. 109°. *Tripropylamine hydrobromide*, m. p. 180°, *auribromide*, m. p. 149°, and *mercuribromide*, m. p. 104°. iso*Butylamine hydrobromide*, m. p. 138°, *auribromide* m. p. 154°, and *mercuribromide*, m. p. 164°. *Di*-iso*butylamine hydrobromide*, m. p. 313°, *auribromide*, m. p. 245°, and *mercuribromide*, m. p. 60°. *Amylamine hydrobromide*, m. p. 243°, *auribromide*, m. p. 105°, and *mercuribromide*, m. p. 213°. *Di*-iso*amylamine hydrobromide*, m. p. about 315°, *auribromide*, m. p. 220°, and *mercuribromide*, m. p. 97°. *Allylamine hydrobromide*, m. p. 91°, and *mercuribromide*, m. p. 115°. *Benzylamine mercuribromide*, m. p. 211°. *Dibenzylamine auribromide*, m. p. 165°, and *mercuribromide*, m. p. 145°. *Pyridine mercuribromide*, m. p. 152°. *Picoline mercuribromide*, m. p. 88°. *Piperidine mercuribromide*, m. p. 143°. E. G.

Hexabromoselenates [Selenibromides]. ALEXANDER GUTBIER and W. GRÜNEWALD (*J. pr. Chem.*, 1912, [ii], **85**, 321—330).—An account of the preparation and properties of the selenibromides of the alkali metals and a number of aliphatic amines of the general formula R_2SeBr_6. The general method of preparation consists in the addition of an aqueous solution of the alkali bromide or of the amine in hydrobromic acid to an excess of a solution of the compound H_2SeBr_6 in hydrobromic acid. The latter solution was prepared by adding bromine to a mixture of finely divided selenium and strong hydrobromic acid. The selenibromides are stable towards air, but are decomposed by water; those of the alkali metals crystallise in octahedra or cubes, belonging to the regular system [LENK.]. In addition to the selenibromides of sodium, potassium, caesium, rubidium, ammonium and of methylamine, dimethylamine, trimethylamine and ethylamine, all of which have been previously isolated (Muthmann and Schäfer, Abstr., 1893, ii, 318; Norris, Abstr., 1898, i, 510; Lenher, Abstr., 1899, ii, 18), the following new compounds are described: *Diethylammonium selenibromide*, $(NH_2Et_2)_2SeBr_6$, lustrous, brownish-red needles of monoclinic habit; the corresponding *propylamine* compound, $(NH_3Pr^{\alpha})_2SeBr_6$, ruby-red plates of a metallic lustre and rhombic habit; *butylammonium selenibromide*, $(NH_3{\cdot}C_4H_9)_2SeBr_6$, forms lustrous, orange-red leaflets; the iso*butylamine* compound, vivid red, hexagonal platelets. *Ethylenediammonium selenibromide*,

$$(C_2H_{10}N_2)SeBr_6,$$

forms garnet-red crystals of a metallic lustre, belonging to the

triclinic system; the *propylene* compound, $(C_3H_{12}N_2)SeBr_6$, garnet-red crystals of rhombic habit. F. B.

Action of Tetraiodoethylene on Organic Bases. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1912, **34**, 290—293).—In earlier papers (Dehn, Abstr., 1911, i, 829; Dehn and Dewey, 1911, i, 914) it was stated that carbon tetrabromide and di-iodoacetylene combine with organic bases, dissolved in dry ether, to form molecular compounds. It is now shown that tetraiodoethylene behaves in a similar manner. Sunlight is generally necessary to promote the reactions. The compounds are decomposed by water; in the case of the diethylamine compound the main reaction is $NHEt_2,C_2I_4 \longrightarrow NHEt_2 + C_2I_4$, but a large proportion decomposes, thus: $3NHEt_2,C_2I_4 + 3H_2O \longrightarrow 3NHEt_2,HI + 3C_2I_2 + 2HI + HIO_3$. Although the normal course of the reaction between tetraiodoethylene and organic bases is that indicated, secondary reactions take place involving the production of di-iodoacetylene, thus: $3NHEt_2 + 2C_2I_4 \longrightarrow 2NHEt_2,HI + 2C_2I_2 + NHEt_2,I_2$, and $3NHEt_2 + 3C_2I_4 \longrightarrow NHEt_2,HI + NHEt_2,I_2 + NHEt_2,HI,I_2 + 3C_2I_2$. The crystalline mass precipitated from the ethereal solution is, therefore, usually a mixture of two or more substances which are sometimes very difficult to separate. The following compounds are described.

The ethylamine *compounds*, NH_2Et,C_2I_4, m. p. 155°, and $NH_2Et,2C_2I_4$, m. p. 133°; *ethylamine hydriodide*, m. p. 167°, and *mercuri-iodide*, m. p. 136°. The diethylamine *compound*, $NHEt_2,C_2I_4$, m. p. 158°; *diethylamine hydriodide*, m. p. 165°, and *mercuri-iodide*, m. p. 115°. The triethylamine *compound*, $NEt_3,2C_2I_4$, m. p. 132°; *triethylamine hydriodide*, m. p. 173° (decomp.), and *mercuri-iodide*, m. p. 84°. The *iso*propylamine *compound*, $NH_2Pr^\beta,2C_2I_4$, m. p. 160°. The dipropylamine *compound*, $NHPr^\alpha{}_2,2C_2I_4$, m. p. 130°; *dipropylamine hydriodide*, m. p. 229° (decomp.), and *mercuri-iodide*, m. p. 81°. The di-*iso*amylamine *compound*, $NH(C_5H_{11})_2,C_2I_4$, m. p. 150°; *di*-iso-*amylamine mercuri-iodide*, m. p. 110°. The benzylamine *compound*, $CH_2Ph\cdot NH_2,C_2I_4$, m. p. 115°; *benzylamine hydriodide*, m. p. 162°, and *mercuri-iodide*, m. p. 134°. The ω-phenylethylamine *compound*, $C_2H_4Ph\cdot NH_2,C_2I_4,C_2I_2$, m. p. 138° (decomp.); *ω-phenylethylamine hydriodide*, m. p. 267°, and *mercuri-iodide*, m. p. 131°. The piperidine *compound*, $C_5H_{11}N,2C_2I_4$, m. p. 147°; *piperidine hydriodide*, softening at 172°, and *mercuri-iodide*, m. p. 104°. The quinoline *compound*, C_9H_7N,C_2I_4, m. p. 132°. The acetamide *compound*, NH_2Ac,C_2I_4,I, m. p. 175°.

Precipitates were also obtained with pyridine, triphenylphosphine, triethylstibine, *p*-phenylenediamine, collidine, and picoline. E. G.

New Compound of Hexamethylenetetramine with Orthoarsenic Acid. GUIDO ROSSI (*Giorn. Farm. Chim.*, 1911, **60**. Reprint 8 pp.)—On mixing saturated alcoholic solutions of orthoarsenic acid and hexamethylenetetramine, the *compound*,

$$(C_6H_{12}N_4)_3,(H_3AsO_4)_2,$$

is obtained. It crystallises in transparent needles, m. p. 173—174°, and (from experiments with a rabbit) is much less toxic than arsenic acid. R. V. S.

Stereoisomerism of Internally Complex Salts: Stereoisomeric Cobaltic Salts of α-Amino-acids. HEINRICH LEY and H. WINKLER (*Ber.*, 1912, 45, 372—377).—The electrical conductivity of solutions of the stereoisomeric cobaltiglycines (Abstr., 1909, i, 886) is extremely small, but still capable of being measured. The results show that the dissociation of these compounds is hardly appreciable. When dissolved in 0·01*N*-sulphuric acid the conductivity of the solution is practically identical with that of the pure acid, indicating that the amino-group is completely saturated by the internal complex formation.

Experiments in which the rate of dehydration of the red and violet isomeric cobaltiglycines has been measured show that the violet isomeride loses its water of crystallisation the more readily.

Using a method similar to that described for the cobaltiglycines (*loc. cit.*), isomeric *cobalti-α-alanines*, $Co(C_3H_6O_2N)_3$, have been prepared from alanine and cobaltic hydroxide. The violet isomeride crystallises in prisms, whilst the red isomeride forms microscopic needles. Both forms are very stable, dissolving in acids, for example, in concentrated sulphuric acid, without decomposition. The absorption spectra of the solutions are practically identical with those of the cobaltiglycines.

The isomeric dinitrotetramminecobaltic salts (flavo- and croceo-salts) cannot be transformed directly one into the other, as is also the case with the above complex compounds. The absorption spectra of dilute solutions of the chloride and nitrate are also practically identical, the only difference being that the croceo-salt gives an additional band in the extreme ultra-violet. T. S. P.

Internally Complex Salts of Platinum and Chromium. HEINRICH LEY and K. FICKEN (*Ber.*, 1912, 45, 377—382).—When a solution of potassium platinochloride is boiled with an excess of glycine, colourless crystals of *platinoglycine*, $Pt(C_2H_4O_2N)_2$, are obtained; they are sparingly soluble in hot water, and soluble in concentrated sulphuric acid. The stability of this compound points to the formation of an internally complex salt, namely,

$$CH_2{<}^{CO_2^-}_{NH_2}{>}Pt{<}^{CO_2^-}_{NH_2}{>}CH_2.$$

Platino-α-alanine, $Pt(C_3H_6O_2N)_2$, is similarly prepared from alanine, and forms glistening, white leaflets, If, however, an excess of alanine is not used (1 mol. of potassium platinochloride to 2 mols. of alanine), a yellow solution is obtained after heating for several hours, which, on precipitation with alcohol, gives yellow needles of *potassium platinochloroalanine*, $K\left[{}^{Cl}_{Cl}{>}Pt{<}^{CO_2^-}_{NH_2}{>}C_2H_4\right]$, which are fairly readily soluble in water. An analogous glycine compound can also be obtained.

If 1 mol. of the green or violet chromium chloride is heated in aqueous solution with 3 mols. of glycine, and 3 mols. of sodium hydroxide gradually added, a dark red solution is obtained, from which violet crystals of *chromiglycine*, $Cr(C_2H_4O_2N)_2\cdot OH,\frac{1}{2}H_2O$, separate. If these are collected from the hot solution, and the filtrate concen-

trated in a vacuum over sulphuric acid, a further quantity of violet crystals is deposited, together with larger, red crystals, having the composition $Cr(C_2H_4O_2N)_3,H_2O$. The red are heavier than the violet crystals, from which they are readily separated by levigation with alcohol. Chromium-pentammine chloride can be used instead of chromium chloride in the above preparation. Both the red and violet salts are sparingly soluble in water and the usual organic solvents. On prolonged boiling with water, the red salt apparently changes into the violet salt. With concentrated sulphuric acid, they give red solutions, which, in contradistinction to those of the cobaltiglycines, gradually decompose with the formation of chromic sulphate. The violet salt is either an hydroxoaquo-salt, $Cr(C_2H_4O_2N)_2\cdot OH\cdot OH_2$, or, more probably, an internally complex salt,

$$(C_2H_4O_2N)_2Cr{<}{}^{OH}_{OH}{>}Cr(C_2H_4O_2N)_2.$$

Similar compounds are obtained when α-alanine is used in place of glycine, the *red* salt being $Cr(C_3H_6O_2N)_3$, and the *violet* salt, $Cr(C_3H_6O_2N)_2OH,H_2O$.

Other amino-acids give similar compounds, which are to be described in another paper. T. S. P.

Adaline. KARL W. ROSENMUND and F. HERRMANN (*Ber. deut. pharm. Ges.*, 1912, **21**, 96—103. Compare Abstr., 1911, i, 118; ii, 1120).—It is shown that, on treatment with boiling water, hot alkaline solution or pyridine, adaline (α-bromo-α-ethylbutyrylcarbamide), $CBrEt_2\cdot CO\cdot NH\cdot CO\cdot NH_2$, yields *diethylhydantoin*, $NH{<}{}^{CEt_2\cdot CO}_{CO-NH}$, colourless crystals, m. p. 181—182°, and that when alkaline solutions are used some *ethylcrotonylcarbamide*, $CH_3\cdot CH\colon CEt\cdot CO\cdot NH\cdot CO\cdot NH_2$, m. p. 91°, is also formed, together with a high-boiling *oil*, $C_{13}H_{20}O_6N_2$, b. p. 283—286°, which probably contains two adaline residues.

T. A. H.

Reduction of Aliphatic Amides and Esters by the Metal-Ammonias. E. CHABLAY (*Compt. rend.*, 1912, **154**, 364—366).—Aliphatic amides decolorise solutions of sodium in liquid ammonia at −50°, forming a mixture of sodium alkyloxide and the sodium derivative of the amide. A similar reaction occurs with esters, the same products being formed. The reaction in the latter case is represented by the equations (1) $R\cdot CO_2R' + 2Na,NH_3 = R\cdot CO\cdot NHNa + R'ONa + NH_3 + H_2$; (2) $R\cdot CO\cdot OR' + 2Na,NH_3 + H_2 = R\cdot CH_2\cdot ONa + R'ONa + 2HN_3$.

W. O. W.

Ureabromin. ARTHUR BILTZ (*Pharm. Zentr.-h.*, 1912, **53**, 245—246).—This name is applied to a molecular combination of carbamide and calcium bromide, $CaBr_2,4CO(NH_2)_2$, prepared by mixing the two components in solution. It is readily soluble in alcohol or water, insoluble in ether, light petroleum or benzene, and melts at 186°. It gives all the ordinary reactions of its components when dissolved in water. It is proposed to use it in medicine as a substitute for alkali bromides. T. A. H.

Reactions of Methylene. III. Diazomethane. Hermann Staudinger and Otto Kupfer (*Ber.*, 1912, 45, 501—509. Compare Abstr., 1911, i, 702, 751).—During the course of some unsuccessful experiments for the preparation of cyano-*iso*nitrile and of di-*iso*-cyanogen, diazomethane has been obtained in 25% yield by the slow addition of chloroform ($1\frac{1}{4}$ mol.) in absolute alcohol to a hot alcoholic solution of potassium hydroxide (4 mols.) and hydrazine (1 mol.). A slow stream of nitrogen is passed through the apparatus during the preparation, whereby the diazomethane is removed and absorbed in ether. Methylhydrazine is a by-product of the reaction.

Pure diazomethane has b. p. $-24°$ to $-23°$ and m. p. $-145°$, and is extremely dangerously explosive, spontaneously or by contact with iodine, grease, etc. In dilute ethereal solution, however, it can be ignited without exploding. When carbon monoxide is passed through ethereal diazomethane and the gaseous mixture is heated at 400—500° in a quartz tube, the methylene produced by the decomposition of the diazomethane reacts with the carbon monoxide to form keten, which is detected by passing the issuing gases into ethereal aniline, whereby acetanilide is produced.

Benzoylhydrazine, potassium hydroxide, and chloroform react in hot alcohol to form about 3% of diazomethane, the main product being benzoic acid, obtained from the intermediately formed phenylketen. Phenylhydrazine is scarcely attacked by potassium hydroxide and chloroform in hot alcohol, but *as*-diphenylhydrazine is converted into benzophenone in 60% yield. C. S.

Urethane and Mercuric Acetate. A. Pieroni (*Gazzetta*, 1911, 41, ii, 754—756).—*Mercurimethylurethane hydroxide*

$$CO_2Me \cdot NH \cdot Hg \cdot OH,$$

is obtained by treating an alcoholic solution of equimolecular quantities of methylurethane and mercuric acetate with a slight excess of alcoholic potassium hydroxide. *Mercurimethylurethane acetate*, $CO_2Me \cdot NH \cdot Hg \cdot C_2H_3O_2$, is prepared by dissolving equimolecular quantities of methylurethane and mercuric acetate in a little water at 60°. On keeping the solution over calcium oxide the substance separates out in crusts of microscopic needles. When treated with alcoholic potassium hydroxide, it decomposes almost quantitatively according to the equation: $CO_2Me \cdot NH \cdot Hg \cdot C_2H_3O_2 + 2KI + H_2O = HgI_2 + CO_2Me \cdot NH_2 + C_2H_3O_2K + KOH$.

Mercuriethylurethane, $CO_2Et \cdot NHg$, is deposited from a solution of ethylurethane and mercuric acetate in water; it forms crusts of microscopic needles, containing 1 mol. H_2O, which it loses in a vacuum over sulphuric acid.

*Mercuri-*iso*amylurethane*, $CO(OC_5H_{11}) \cdot NHg$, is obtained by keeping an alcoholic solution of equimolecular quantities of *iso*amylurethane and mercuric acetate; it forms crystalline crusts, m. p. about 165° (decomp.). With sodium iodide, it decomposes in the same way as mercurimethylurethane acetate. R. V. S.

Decomposition of Pyrazoline Bases as a means of Obtaining Derivatives of *cyclo*Propane. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 165—180).—The conversion into the

dicyclic hydrocarbon, carane, of the base obtained by the action of hydrazine on tanacetone (compare Abstr., 1911, i, 1028) seemed to indicate that the formation of the trimethylene ring was related to the formation of the base. Since mesityl oxide, a compound structurally very similar to pulegone, also reacts with hydrazine to form a compound which gives 1 : 1 : 2-trimethyl*cyclo*propane on decomposition, it was at first thought that the product of the interaction of mesityl oxide and hydrazine was not a pyrazoline derivative, as Curtius supposed, but a compound having the structure:

$$CH{\large<}\begin{matrix}-CMe_2-\\ N(NH_2)\end{matrix}{\large>}CMe\cdot$$

Further investigation has shown, however, that this compound is really a pyrazoline derivative, as also is the base formed by pulegone with hydrazine, this having the constitution:

$$\begin{matrix}CH_2\text{——}CH_2\cdot CH\cdot CMe_2\\ CHMe\cdot CH_2\cdot C\text{====}N\end{matrix}{\large>}NH,$$

and not that previously given (*loc. cit.*). The decomposition of this compound into carane and nitrogen is exactly similar to that of 3 : 5 : 5-trimethylpyrazoline (from mesityl oxide and hydrazine) into 1 : 1 : 2-trimethyl*cyclo*propane and nitrogen, the two nitrogen atoms being eliminated from the pyrazole nucleus and the residue closing up to a three carbon-atom ring. Similar decompositions take place with 1-methyl-1 : 2-diethylpyrazoline, which yields 1-methyl-1 : 2-diethyl*cyclo*propane, and with esters of pyrazoline-3 : 4 : 5-tricarboxylic acid, which yield esters of *cyclo*propanetricarboxylic acids (compare Buchner, Abstr., 1888, 1274; 1890, 736).

The author intends to ascertain whether derivatives of *cyclo*propanone can be obtained in a similar manner from pyrazolone compounds.

1 : 1 : 2-Trimethyl*cyclo*propane, C_6H_{12}, obtained by heating 3 : 5 : 5-trimethylpyrazoline in a sealed tube with potassium hydroxide and platinised porous tile, is a liquid, b. p. 52·5°/752 mm., 52·6°/753 mm., 52·8°/756 mm., D_0^{20} 0·6949, n_D 1·3866. The compound described under this name by Zelinsky and Zelikoff (Abstr., 1901, i, 657) was apparently not pure, the high value of the molecular refraction indicating considerable admixture of ethylene hydrocarbon. The action of alkaline permanganate on 1 : 1 : 2-trimethyl*cyclo*propane is very slow, but much more rapid than with the dicyclic trimethylene hydrocarbons, thujane and carane, or with the 1-methyl-1 : 2-diethyl*cyclo*propane described below. Fuming nitric acid readily reacts with the hydrocarbon with development of heat, whilst concentrated sulphuric acid polymerises it.

The action of bromine on 1 : 1 : 2-trimethyl*cyclo*propane in acetic acid solution yields: (1) a small proportion of *β-bromo-β-methylpentane*, $CMe_2Br\cdot CH_2\cdot CH_2Me$, b. p. 135—138°/752 mm., D_0^{20} 1·1806, n_D 1·4517, which is the result of a secondary reaction of the hydrogen bromide liberated on the hydrocarbon; (2) *βδ-dibromo-β-methylpentane*, $CMe_2Br\cdot CH_2\cdot CHMeBr$, b. p. 87—89°/23 mm., D_0^0 1·6242, D_0^{20} 1·5979, n_D 1·5097, which yields *β*-methylpentane when reduced with hydrogen

iodide; thus combination of bromine with 1:1:2-trimethyl*cyclo*propane takes place at the least hydrogenated carbon atom.

Reduction of 1:1:2-trimethyl*cyclo*propane by Sabatier's method gives $\beta\beta$-dimethylbutane, so that hydrogen combines with this hydrocarbon at the most highly hydrogenated carbon atom.

The action of fuming hydriodic acid on 1:1:2-trimethyl*cyclo*propane yields: (1) β-iodo-$\beta\gamma$-dimethylbutane, $CMe_2I\cdot CHMe_2$, b. p. 83—84°/77 mm., 141°/755 mm. (slight decomp.), D_0^{20} 1·4435, n_D 1·5035, which seems to be accompanied by a small proportion of another iodo-compound, probably β-iodo-β-methylpentane. The action of fuming hydrobromic acid on 1:1:2-trimethyl*cyclo*propane yields β-bromo-β-methylpentane (see above).

1-*Methyl*-1:2-*diethyl*cyclo*propane*, $CH_2<\begin{matrix}CHEt\\ |\\ CMeEt\end{matrix}$, obtained by heating 5-methyl-3:5-diethylpyrazoline (compare Curtius and Zinkeisen, Abstr., 1899, i, 165) in a sealed tube at 240°, has b. p. 108—109°/742 mm., D_0^{20} 0·7382, n_D 1·4102. It combines slowly with bromine, whilst with hydrobromic acid it gives *γ-bromo-γ-methylheptane* (?), b. p. 101—102°/53 mm., D_0^{20} 1·1406, n_D 1·4613, which, when distilled with aniline, yields an unsaturated *hydrocarbon*, C_8H_{16}, b. p. 117—119°/742 mm., $D_0^{17.5}$ 0·7426, n_D 1·4210, this forming a liquid bromide.

T. H. P.

Loschmidt's Graphic Formulæ: History of the Benzene Theory. RICHARD ANSCHÜTZ (*Ber.*, 1912, 45, 539—553).—Historical. The author gives an account of the graphic formula developed by Loschmidt in his "*Chemische Studien*" (Vienna, 1861). It is pointed out that the latter ascribed a ring structure to the benzene nucleus four years before Kekulé published his benzene theory. F. B.

Stereochemistry of the Aromatic Series. ROMÁN CASARES (*Anal. Fis. Quim.*, 1912, 10, 14—18).—The author proposes a three dimensional formula for benzene based on an alternate arrangement of tetrahedra, in such a way that the projection on a plane is a regular hexagon. The difference from Ladenburg's prism formula is slight, and the same difficulty would be experienced in explaining the mechanism of reduction. Naphthalene, anthracene, phenanthrene, and chrysene are formulated on the same principle. G. D. L.

Hydrogenation and Dehydrogenation. HEINRICH WIELAND (*Ber.*, 1912, 45, 484—493).—The researches of Sabatier, Ipatieff, Knoevenagel, and others show that the addition of hydrogen to an unsaturated organic compound in the presence of finely divided nickel, copper, palladium, etc., at a definite temperature is reversed at a higher temperature. It is to be anticipated, therefore, that Paal's method of reducing substances containing double linkings by hydrogen in the presence of colloidal palladium at the ordinary temperature is reversible, and that, under definite conditions, the same state of equilibrium must be reached whether the unsaturated or the hydrogenised substance is employed initially. The author finds that by shaking with palladium

black (carefully prepared free from oxygen), aqueous quinol is partly converted into *p*-benzoquinone and quinhydrone, hydrazobenzene dissolved in benzene is changed into azobenzene and aniline, dihydronaphthalene dissolved in benzene yields naphthalene and tetrahydronaphthalene, and dihydroanthracene in benzene is slowly transformed into anthracene; acenaphthene and bisdiphenylene-ethane are unchanged under the preceding conditions.

In these reactions the palladium plays the part, not of a catalyst, but of a substance of active mass; by increasing the amount of the metal, the equilibrium of the system is shifted in the direction whereby the yield of the dehydrogenised substance is increased.

Unsaturated substances which decolorise potassium permanganate can, in general, be catalytically hydrogenised, but are not necessarily attacked by nascent hydrogen; naphthalene is unaffected by hydrogen and palladium, but is reduced to dihydronaphthalene by sodium and alcohol, whereas dihydronaphthalene is unaffected by sodium and alcohol, but is easily converted into tetrahydronaphthalene by hydrogen and palladium. It appears, therefore, that the activation of hydrogen in the presence of a finely divided metal is not due to the production of nascent (atomic) hydrogen, but more probably to the formation of a metallic hydride which additively reacts with the unsaturated substance: $R{:}R + PdH_2 \rightleftarrows RH{\cdot}R{\cdot}PdH \rightleftarrows RH{\cdot}RH + Pd$. The probability of the formation of such intermediate additive compounds is supported by the facts that methyl or ethyl alcohol is absorbed by palladium black with development of heat, and the alcohol can only be recovered by long keeping in a vacuum; it then contains a certain amount of the aldehyde. Under such conditions, propyl alcohol is much more readily converted into propaldehyde, whilst benzyl alcohol yields benzaldehyde at once. C. S.

The Addition of Chlorine to Dichlorobenzenes. T. VAN DER LINDEN (*Ber.*, 1912, 45, 411—418. Compare this vol., i, 174).—The author hoped by the removal of two molecules of hydrogen chloride from any dichlorobenzene hexachloride [octachloro*cyclo*hexane] to obtain a substance of the composition $C_6H_2Cl_6$ which might be considered as identical with the assumed intermediate product in the substitution of a chlorine atom into tetrachlorobenzene.

The additive compound of *p*-dichlorobenzene and chlorine was obtained by passing chlorine into a solution of the substance in carbon tetrachloride under strong sodium hydroxide solution in sunlight, also by exposing to sunlight a mixture of the theoretical quantities of *p*-dichlorobenzene and chlorine in a closed tube. The main product (from its resemblance to β-benzene hexachloride) is designated β-*p*-dichlorobenzene hexachloride, and after recrystallisation from nitrobenzene has m. p. 262°; it has already been obtained by Jungfleisch (*Bull. Soc. chim.*, 1868, [2], 9, 352). On treatment with alcoholic potash, three molecules of hydrogen chloride are eliminated with formation of pentachlorobenzene; the same behaviour is exhibited by all the isomerides described below.

The carbon tetrachloride mother liquors of the above substance contained an isomeric hexachloride, which, on account of its low m. p.

and considerable solubility, is termed *α*-p-*dichlorobenzene hexachloride*; the m. p. is 89·6°. Indications of a third isomeride, m. p. 110—120°, were also observed. o-*Dichlorobenzene hexachloride*, obtained by the sealed tube method, has m. p. 147°.

m-*Dichlorobenzene hexachloride* was obtained by the action of chlorine on the dichloro-compound under a layer of dilute sodium hydroxide solution; it has m. p. 81·8°.

As the above substances, even when treated with an insufficiency of alcoholic potash, yield only pentachlorobenzene and unchanged substance, *α*- and *β*-chlorobenzene hexachlorides were prepared by the sealed tube method, but alcoholic potash again removes simultaneously three molecules of hydrogen chloride from each molecule of hexachloride. D. F. T.

Reduction of Nitrobenzene by means of Ferrous Hydroxide. Herman Camp Allen (*J. Physical Chem.*, 1912, 16, 131—169).—The products of reduction of nitrobenzene by ferrous sulphate with slight excess of sodium hydroxide depend on the temperature, concentration, and order of mixing of the reacting substances.

When nitrobenzene is run into a well stirred mixture of ferrous sulphate and sodium hydroxide solutions or when nitrobenzene and ferrous sulphate are stirred together and sodium hydroxide is slowly introduced, the reduction takes place in a neutral or slightly alkaline medium, and the product is mainly aniline. The yield of aniline varies from 100% at room temperature to 80% at the boiling point. A high yield of aniline is also obtained when the ferrous sulphate is added last, if it is run in quickly and in excess.

When, however, sodium hydroxide and nitrobenzene are stirred together, and ferrous sulphate is added very slowly, the reduction takes place in a strongly alkaline medium, and the product is mainly hydrazobenzene. At 75° the yields were: aniline 21%, hydrazobenzene 60%, azoxybenzene 14%. At the boiling point the yields were: aniline 33%, hydrazobenzene 58%. When the ferrous sulphate was restricted to the amount required to reduce to azoxybenzene only, the yields were: aniline 18%, azoxybenzene 76%.

Both azoxybenzene and azobenzene are reduced by excess of alkaline ferrous sulphate at the boiling point, the product being hydrazobenzene with some aniline. Aniline seems to be formed in this way in the alkaline reduction of nitrobenzene at 100°, whereas at the ordinary temperature it is formed by the nitrosobenzene-phenylhydroxylamine route. There is a minimum production of aniline at about 75°, and the utility of alcohol in the electrolytic production of hydrazobenzene and azobenzene is partly due to its solvent action, and partly to its favourable boiling point.

According to Haber's scheme for the reduction of nitrobenzene (Abstr., 1900, i, 281), azoxybenzene is the immediate forerunner of hydrazobenzene, as the above results suggest, and the oxidation of hydrazobenzene by nitrobenzene gives azobenzene, the nitrobenzene being reduced to azoxybenzene at the same time. The author finds that the production of azobenzene from hydrazobenzene on boiling for twenty minutes with excess of nitrobenzene is almost quantitative, and

azoxybenzene is formed simultaneously, in accordance with Haber's view. In the Elbs method of electrolytic preparation of azobenzene, the intermediate stage is probably azoxybenzene, since with a low current density in well stirred solutions, azoxybenzene is the principal product.

In the author's experiments, 1·2 gram of nitrobenzene was reduced and the filtered liquid was extracted with benzene. It was assumed that the extract contained only aniline, hydrazobenzene, azobenzene, azoxybenzene, and unaltered nitrobenzene. The aniline was extracted with dilute sulphuric acid and titrated with bromate. The residue was estimated by evaporating until a more or less sharp bend in the time-weight curve indicated that the last traces of benzene had been removed. A similar procedure gave the residue after aniline and hydrazobenzene had been extracted together by 1 : 3 sulphuric acid; hence hydrazobenzene was calculated by difference. Azobenzene was estimated colorimetrically in the above residue, and nitrobenzene was reduced to aniline and titrated. Azoxybenzene was then calculated by difference. Phenylhydroxylamine was present in traces only.

In neutral or slightly alkaline reductions at the boiling point, about 15% of the nitrobenzene remained unaccounted for. It is suggested that decomposition of the intermediate product, phenylhydroxylamine, may have given rise to substances not extracted by benzene from the aqueous solution. In strongly alkaline reductions at the boiling point, the nitrobenzene could all be accounted for. R. J. C.

Fission of Phenylethyltrimethylammonium [Chloride]. Hermann Emde (*Apoth. Zeit.*, 1912, **27**, 18—19).—The reduction of phenylethyltrimethylammonium chloride by means of sodium amalgam (compare Abstr., 1909, i, 708; this vol., i, 20) results in the formation of trimethylamine and styrene instead of ethylbenzene as previously assumed. In this case, the action of sodium amalgam is precisely similar to that of sodium hydroxide.

Explicit directions are given for the reduction of crude benzyl cyanide to phenylethylamine, and for the transformation of the latter into phenylethyltrimethylammonium chloride by means of methyl sulphate. H. W.

New Derivatives of Indene. Victor Grignard and Charles Courtot (*Compt. rend.*, 1912, **154**, 361—364. Compare Abstr., 1911, i, 193, 292).—The action of bromine on magnesium indenyl bromide gives rise to the formation of 1 : 2 : 3-*tribromoindane*, $C_9H_7Br_3$, m. p. 133—134°, together with an oily substance containing 1-*bromoindene*, C_9H_7Br. The latter is best prepared by adding the organo-magnesium derivative to cyanogen bromide, when it is obtained as a yellow liquid, b. p. 126°/22 mm. The compound resembles allyl bromide in its reactions. If cyanogen chloride is used instead of the bromide, 1-*cyanoindene*, $C_{10}H_7N$, b. p. 140—142°/14 mm., is formed. When treated by Pinner's method, this yields ethyl indene-1-carboxylate, b. p. 140°/8 mm. (compare Weissgerber, Abstr., 1911, i, 1442).

Di-indenyl, $CH{<}{\substack{C_6H_4\\CH}}{>}CH\cdot CH{<}{\substack{C_6H_4\\CH}}{>}CH$, prepared by the

action of iodine on magnesium indenyl bromide in toluene, occurs as colourless crystals, m. p. 99—100°; when treated with bromine it forms two *tetrabromides.* One of these is soluble in chloroform and has m. p. 138—139°, whilst the other is insoluble and has m. p. 222—224°. W. O. W.

The Influence of the Nitro-group on the Sulphonation of Diphenylmethane. ALFRED KLIEGL (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 225–226).—Wedekind and Schenk (Abstr., 1911, i, 190) found it impossible to sulphonate the methylene group of diphenylmethane with chlorosulphonic acid. An attempt has therefore been made to lessen the liability of the nuclei to sulphonation, and at the same time to increase the reactivity of the methylene group by the introduction of substituents. It is found, however, that nitro-groups increase the readiness with which diphenylmethane is sulphonated. In all three nitrodiphenylmethanesulphonic acids, the sulpho-group occupies the para-position in the un-nitrated nucleus. Triphenylmethane behaves in a similar manner, and *o*-nitrotriphenylmethane gives a disulphonic acid with concentrated sulphuric acid on the water-bath.

p-Aminodiphenylmethane-*p*-sulphonic acid yields a sparingly soluble diazosulphonic acid, which behaves as an internal salt, although the two salt-forming groups are attached to different nuclei. C. H. D.

Sulphonation of β-Nitronaphthalene. HANS KAPPELER (*Ber.*, 1912, **45**, 633—635).—The sulphonation of β-nitronaphthalene with fuming sulphuric acid is completely analogous to that of β-naphthylamine. A mixture of two monosulphonic acids is obtained, which were identified by reduction to the corresponding β-naphthylaminesulphonic acids.

2-*Nitronaphthalene*-5-*sulphonyl chloride* forms large, pale yellow prisms, m. p. 127°; the corresponding *amide* crystallises in yellow, four-and six-sided plates, m. p. 223—224°.

2-*Nitronaphthalene*-8-*sulphonyl chloride* separates in tiny, almost colourless needles, m. p. 169—170°; the *amide* forms colourless, crystalline tablets, m. p. 261—262°.

The free *sulphonic acids* were obtained as colourless, microcrystalline precipitates. E. F. A.

Action of Sulphurous Acid on Aldehydoaminic Bases. MARIO MAYER (*Gazzetta*, 1912, **42**, i, 50—56. Compare Abstr., 1911, i, 223).—*Benzylideneaniline anhydrosulphite*,

$$(CHPh{:}NPh)_2,SO_2,$$

is an orange-yellow powder, m. p. 115—120° (decomp.), which is obtained when dry sulphur dioxide acts on dry benzylideneaniline, and also (more easily) when a benzene solution of benzylideneaniline is saturated with sulphur dioxide. The substance loses sulphur dioxide when kept, leaving benzylideneaniline as the only product.

Aniline benzylideneaniline sulphite, already obtained by Knoevenagel, can also be prepared by saturating an ethereal solution of benzylideneaniline with sulphur dioxide. When it is heated in a

sealed tube for some hours at 105—110°, aniline and aniline sulphite are formed, and, in addition, *benzylideneaniline hydrogen sulphite*, $C_{13}H_{13}O_3NS$. This decomposition renders improbable Eibner's supposition (Abstr., 1901, i, 376) that the original compound is dianilinophenylmethane anhydrosulphite, $CHPh(NHPh)_2,SO_2$. Benzylideneaniline hydrogen sulphite is best prepared by passing sulphur dioxide through a very dilute aqueous-alcoholic solution of benzylideneaniline; it forms tufts of acicular crystals, m. p. 145°. If the solution is more concentrated, the salt of m. p. 125° is obtained, but when this is removed, the liquid slightly warmed, and treated with more sulphur dioxide, a substance separates in the form of long, flat needles, m. p. 147°, which are identical in behaviour with those above mentioned, m. p. 145°. Benzylideneaniline hydrogen sulphite yields the above-mentioned salt of m. p. 125° when treated with aniline.

Speroni (Abstr., 1903, i, 246) obtained the neutral anhydrosulphite of aniline and benzaldehyde, giving the m. p. 138—140°. On repeating this preparation the author obtains a substance, m. p. 125°, which is identical with Knoevenagel's salt previously referred to. If, however, this compound is treated with warm alcohol, the greater part of it then has m. p. 140° (decomp.) and gives the same analytical figures as the salt of m. p. 125°, and it is suggested that the two substances are the aniline salts of two isomeric forms of the sulphurous acid. Speroni, by treating a neutral aqueous solution of aniline sulphite with benzaldehyde, obtained a substance, m. p. 130°, but the author, working under the same conditions, always obtains a product, m. p. 125—127°, identical with the salt of m. p. 125° already mentioned.

When the three compounds above described (of m. p. 115—120°, 145° and 125° respectively) are treated with a cold, saturated, alcoholic solution of picric acid, the first two yield benzylideneaniline picrate, whilst the third gives also aniline picrate.

In regard to the constitution of the sulphites described in this and in the earlier paper, the author rejects Eibner's view (*loc. cit.*) that all compounds formed from aldehydes, amines, and sulphurous acid are sulphites of aldehydoaminic bases. Such substances as the additive products from benzylideneaniline and sulphur dioxide or sulphurous acid do belong to that type, but the other compounds described in the present paper and the aldehydo- and keto-sulphites of the alkaloids do not. The aldehydoaminic bases which are obtained when some of these decompose are not present in the compounds themselves, but are formed by the interaction of the aldehyde and amine first formed in the decomposition.

R. V. S.

Electrolysis of Phenyldialkylhydroxyethylammonium Iodides and Some Derivatives of Choline. BRUNO EMMERT (*Ber.*, 1912, 45, 430—433).—The electrolysis of quaternary phenylammonium salts at lead cathodes leads to the formation of tertiary aliphatic amines (Abstr., 1909, i, 376, 602). An attempt has been made to extend this method to those cases in which unsaturated aliphatic and

hydroxyalkyl groups are attached to the *N*-atom. By the electrolysis of phenyldimethylallylammonium iodide, however, propylene and dimethylaniline were obtained in good yield, the allyl instead of the phenyl group being eliminated. Electrolysis of phenyldimethylhydroxyethylammonium iodide and of phenylmethylethylhydroxyethylammonium iodide yielded dimethyl-β-hydroxyethylamine and methylethyl-β-hydroxyethylamine, whilst, at the same time, a certain amount of a tertiary aniline was formed, one aliphatic group being split off.

Dimethyl-β-hydroxyethylamine was dried over potassium hydroxide and barium oxide, and, whilst still somewhat moist, had b. p. 129—133°. Ladenburg (Abstr., 1882, 166) found 130—134°, and Knorr (Abstr., 1889, 905) 128—130°. The *gold* salt was analysed.

Methylethyl-β-hydroxyethylamine, isolated through its *hydrochloride*, had b. p. 149—150°. The *aurichloride* was analysed. When treated with methyl iodide in ethereal solution, it formed *dimethylethyl-β-hydroxyethylammonium iodide*, which, on treatment with moist silver oxide, yielded the corresponding base. The latter was identified by conversion into its *aurichloride*, m. p. 276—277° (decomp.). Methylethyl-β-hydroxyethylamine and ethyl iodide reacted to form an iodide, from which methyldiethyl-β-hydroxyethylammonium hydroxide was prepared. The *aurichloride* obtained from the latter had m. p. 246—247° (decomp.).

A similar series of compounds was obtained from methylethyl-β-hydroxyethylamine and propyl iodide. In this case the corresponding *aurichloride* could not be obtained in a crystalline state. The *platinichloride*, $C_{16}H_{40}O_2N_2Cl_6Pt$, was analysed. H. W.

Diphenylhydroxylamine. HEINRICH WIELAND and ALEXANDER ROSEEU (*Ber.*, 1912, **45**, 494—499).—The interaction of nitrosobenzene and magnesium phenyl bromide in ether at $-15°$ under carefully regulated conditions leads to the formation of *$\beta\beta$-diphenylhydroxylamine*, $NPh_2\cdot OH$, m. p. 60° (decomp.), colourless crystals. The substance, when pure, can be kept for eight days without decomposition, develops a deep blue coloration with concentrated sulphuric acid, is neutral in character, reduces ammoniacal silver solutions in the cold, and yields diphenylamine by reduction. It reacts with diphenylhydrazine hydrochloride (0·5 mol.) in slightly acidified alcohol to form the hydrochloride of quinoneanildiphenylhydrazone (Abstr., 1911, i, 82), the constitution of which is thus definitely settled. C. S.

Action of Bromine in Presence of Aluminium Bromide on the Methyl*cyclo*hexanols. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1912, **154**, 521. Compare Abstr., 1911, i, 779).—The three methyl*cyclo*hexanols behave similarly to *cyclo*hexanol in their behaviour towards bromine in presence of aluminium bromide. In each case the solid pentabromotoluene is formed, together with a yellow oil. The latter is a mixture of bromo-derivatives, and is capable of undergoing further bromination, giving gummy products in the case of methyl*cyclo*hexan-2- and -4-ol. The third isomeride, however, gave a small quantity of *hexabromomethyl*cyclo*hexane*, $C_7H_8Br_6$, in the form of long, colourless needles, m. p. 295°. W. O. W.

Halogen Derivatives of Phenolic Ethers. ALPHONSE MAILHE and MARCEL MURAT (*Compt. rend.*, 1912, **154**, 601—604 *).—The catalytic method, in which thorium oxide is employed, is very advantageous for the preparation of diphenyl ether and its homologues, which are obtained with difficulty by the ordinary processes.

p-*Chlorodiphenyl ether*, $OPh\cdot C_6H_4Cl$, prepared by the action of chlorine in presence of iodine on diphenyl ether in carbon tetrachloride solution, has b. p. 284°/760 mm., D^{15} 1·2026, n_D 1·599 ; *di*-p-*chlorodiphenyl ether*, $O(C_6H_4Cl)_2$, formed at the same time has b. p. 312—315°. p-*Bromodiphenyl ether* has b. p. 305°, and the dibromo-derivative, m. p. 54°, b. p. 338—340°. Di-*o*-tolyl ether gave the following compounds : a *monochloro*-derivative, b. p. 308—310°, a *dichloro*-derivative, b. p. 338—340°, a *monobromo*-derivative, b. p. 330°/670 mm., D^{10} 1·4162. Di-*p*-tolyl ether gave a *monochloro*-derivative, b. p. 315°/760 mm., a *dichloro*-derivative, b. p. 240—245°/20 mm., D^{10} 1·1800, a *monobromo*-derivative, b. p. 330—333°/760 mm., D^{10} 1·417, and a *dibromo*-derivative, m. p. 131°. W. O. W.

Action of Bromine and Chlorine on Dehydrodicarvacrol. HENRI COUSIN (*Compt. rend.*, 1912, **154**, 441—443 ; *J. Pharm. Chim.*, 1912, [vii], **5**, 236—240.† Compare Abstr., 1910, i, 476).—*Dibromodehydrodicarvacrol*, $C_{20}H_{24}O_2Br_2$, prepared by the action of bromine on dehydrodicarvacrol in chloroform solution, occurs in pale yellow prisms, m. p. 179—180° (corr.). The corresponding *dichloro*-derivative, obtained by using the calculated amount of chlorine, crystallises in pale yellow prisms. When excess of chlorine is employed, *dichlorodehydrodicarvacroquinone tetrachloride*, $C_{20}H_{22}O_2Cl_6$, is formed as a yellow resin, slowly changing to crystals, m. p. 155—156° (decomp.). When treated with reducing agents, this substance yields dichlorodehydrodicarvacrol ; the corresponding quinone has not been isolated. W. O. W.

Colour of Alkaline Solutions of Quinol and of Their Oxidation Products. ROBERT LUTHER and A. LEUBNER (*J. pr. Chem.*, 1912, [ii], **85**, 233—234).—On treatment with aqueous alkalis, quinone gives yellowish-green solutions, which become brownish-black on exposure to air. Addition of sodium sulphite to solutions of quinone produces an intensely greenish-blue coloration, which gradually changes to light yellow. When shaken with air, the yellow solutions become green and then light yellow. If the traces of oxidation-products formed by dissolving the quinone are destroyed by potassium hydrogen sulphite or quinol, the addition of sodium sulphite produces a brown coloration. The blue coloration is probably due to the formation of an alkali salt of an oxidation product of quinone.

According to Euler and Bolin (Abstr., 1909, ii, 374) quinol dissolves in alkalis, yielding yellow solutions, owing to the formation of quinonoid salts. The authors find, however, that solutions of potassium carbonate or potassium hydroxide and of quinol, to which small quantities of sodium hydrogen sulphite have been added in

* and *Bull. Soc. chim.*, 1912, [iv], **11**, 328—332.
† and *Bull. Soc. chim.*, 1912, [iv], **11**, 332—336.

order to destroy dissolved oxygen and traces of quinone, do not yield yellow colorations when mixed, but gradually acquire a dark brown colour on exposure to air. From these observations the conclusion is drawn that salts of quinol, quinone, hydroxyquinol, and dihydroxyquinol are respectively colourless, yellow, bluish-green, and reddish-brown. F. B.

Isomerism Among the Ethers of Di*iso*eugenol. ERNESTO PUXEDDU (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 124—129. Compare Abstr., 1909, i, 225).—The author considers it probable that the polymerisation of eugenol ethyl ether observed by Wassermann is preceded by an isomerisation, so that Wassermann's polymeride is a di*iso*eugenol diethyl ether, stereoisomeric with the di*iso*eugenol diethyl ether described by the author (*loc. cit.*). They differ not only in solubility and in m. p., but also give different bromine derivatives. Eugenol ethyl ether was prepared by the action of ethyl sulphate on eugenol dissolved in potassium hydroxide (10%), and also by Wassermann's method. When it was distilled, the residue which did not distil at 260° consisted of Wassermann's polymeride, but had m. p. 140° (Wassermann gave 125°). It is obtained in better yield by heating eugenol ethyl ether for fifteen hours in a bath at about 270°. In chloroform solution, it absorbs bromine, but no individual substance could be isolated from the product. The di*iso*eugenol diethyl ether previously described by the author, when treated with bromine in ethereal solution cooled with ice and salt, yields *monobromodiiso-eugenol diethyl ether*, $C_{24}H_{31}O_4Br$, which forms yellowish-green, rhombohedral crystals, m. p. 118°. R. V. S.

Iodothio-ethers, Iodosulphones, Iodosulphonic Esters, and their Derivatives with Multivalent Iodine. CONRAD WILLGERODT and MAX KLINGER (*J. pr. Chem.*, 1912, [ii], 85, 189—198).—p-*Iodothiophenetole* (p-*iodophenyl ethyl sulphide*), $C_6H_4I{\cdot}SEt$, prepared by reducing *p*-nitrothiophenetole (*p*-nitrophenyl ethyl sulphide) with tin and hydrochloric acid and replacing the amino-group of the resulting p-*aminothiophenetole* (p-*aminophenyl ethyl sulphide*) by iodine by means of the diazo-reaction, is a yellow oil, b. p. 146—147°/11 mm. When treated with chlorine in chloroform solution, it yields an unstable *iododichloride*, which rapidly decomposes into *p*-iodothiophenetole and p-*iodobenzenesulphonyl chloride*. The formation of the latter compound is considered to be due to the decomposition of the iododichloride into ethyl chloride and the compound (I), which then reacts with the iodoso-compound (II), produced by the action of moisture on the iododichloride:

(I) $C_6H_4I{\cdot}SCl + $ (II) $2SEt{\cdot}C_6H_4{\cdot}IO = 2C_6H_4I{\cdot}SEt + C_6H_4I{\cdot}SO_2Cl$.

Methyl p-*iodobenzenesulphonate*, prepared from the sulphonyl chloride and methyl alcohol, crystallises in rhombohedra, m. p. 74°. It yields a yellow, crystalline *iododichloride*, $ICl_2{\cdot}C_6H_4{\cdot}SO_3Me$, which is converted by aqueous sodium carbonate into *methyl* p-*iodosobenzenesulphonate*, $IO{\cdot}C_6H_4{\cdot}SO_3Me$ (decomp. 176—178°); the *iodosoacetate*, $I(OAc)_2{\cdot}C_6H_4{\cdot}SO_3Me$, forms rhombic prisms, m. p. 174°. *Methyl* p-*iodoxybenzenesulphonate* is prepared by the action of sodium hypochlorite and acetic acid on the iododichloride.

p-*Iodophenylethylsulphone*, $C_6H_4I \cdot SO_2Et$, obtained as a white powder, m. p. 83°, by oxidising *p*-iodothiophenetole with chromium trioxide in glacial acetic acid solution, yields an *iododichloride*, $ICl_2 \cdot C_6H_4 \cdot SO_2Et$ (decomp. 118°), which is converted by the usual methods into p-*iodosophenylethylsulphone* (decomp. 235°), the *iodosoacetate*,

$$I(OAc)_2 \cdot C_6H_4 \cdot SO_2Et,$$

monoclinic needles, m. p. 167—170°, and p-*iodoxyphenylethylsulphone*, $IO_2 \cdot C_6H_4 \cdot SO_2Et$, which crystallises in small octahedra, exploding at 220°.

p-*Iododiphenyl sulphide*, $C_6H_4I \cdot SPh$, prepared from *p*-aminodiphenyl sulphide (Kehrmann and Bauer, Abstr., 1897, i, 27) by means of the diazo-reaction, crystallises in lustrous, white leaflets, m. p. 35°, b. p. 230°/11 mm. Attempts to prepare the iododichloride by the action of chlorine in chloroform solution yielded a yellow oil, which on exposure to air is transformed into p-*iododiphenyl sulphoxide*,

$$C_6H_4I \cdot SOPh,$$

and p-*iododiphenylsulphone*, $C_6H_4I \cdot SO_2Ph$. The last-mentioned compound has also been prepared (1) by oxidation of *p*-iododiphenyl sulphide with chromium trioxide in glacial acetic acid solution, and (2) by the interaction of *p*-iodobenzenesulphonyl chloride and benzene in the presence of aluminium chloride. It crystallises in white needles, m. p. 141°, and forms an *iododichloride*, $ICl_2 \cdot C_6H_4 \cdot SO_2Ph$, rhombic crystals (decomp. 130°). p-*Iodosodiphenylsulphone* is a pale yellow powder (decomp. 210°); the *iodosoacetate*, $I(OAc)_2 \cdot C_6H_4 \cdot SO_2Ph$, forms white needles (decomp. 195°); p-*iodoxydiphenylsulphone*,

$$IO_2 \cdot C_6H_4 \cdot SO_2Ph,$$

crystallises in white leaflets, which explode at 220—223°.

p-Iododiphenylsulphoxide, prepared by oxidising a cold glacial acetic acid solution of *p*-iododiphenyl sulphide with aqueous chromic acid, forms large, white, rhombic crystals, m. p. 106°. F. B.

Iodosulphones and Their Derivatives with Multivalent Iodine. CONRAD WILLGERODT and MAX PLOCKSTIES (*J. pr. Chem.*, 1912, [ii], 85, 198—207).—p-*Iodophenyl*-p-*tolylsulphone* (4-*iodo*-4′-*methyldiphenylsulphone*), $C_6H_4Me \cdot SO_2 \cdot C_6H_4I$, is prepared by the interaction of *p*-iodobenzenesulphonyl chloride and toluene in carbon disulphide solution in presence of aluminium chloride; it crystallises in rhombs, m. p. 162°, and yields an *iododichloride*, which crystallises in slender, sulphur-yellow needles (decomp. 120°), and forms with pyridine an *additive* compound,

$$C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot ICl_2, 2C_5H_5N,$$

decomposing at 118—120°.

4-*Iodosophenyl*-p-*tolylsulphone* is a pale yellow powder (decomp. 197°); the *iodosoacetate*, $C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot I(OAc)_2$, crystallises in lustrous needles, decomposing at 180°. 4-*Iodoxyphenyl*-p-*tolylsulphone*, $C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot IO_2$, forms a white powder (decomp. 320°), and reacts with 4-iodosophenyl-*p*-tolylsulphone and silver oxide in the presence of water, yielding *di*-p-4-*toluenesulphonylphenyliodinium hydroxide*, $OH \cdot I(C_6H_4 \cdot SO_2 \cdot C_6H_4Me)_2$, which was obtained only in aqueous solution, and forms a yellow iodide.

p-4-*Toluenesulphonyldiphenyliodinium chloride*,
$C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot IPhCl$,
is obtained in aqueous solution by heating phenyl-*p*-tolylsulphone-4′-iododichloride with mercury diphenyl and water at 50°; the *iodide* (decomp. 132°) and *platinichloride*, slender, yellow needles (decomp. 178°), are described.

4-*Iododiphenylsulphone*-4′-*carboxylic acid*, $C_6H_4I \cdot SO_2 \cdot C_6H_4 \cdot CO_2H$, prepared by the oxidation of 4-iodophenyl-*p*-tolylsulphone with chromium trioxide in glacial acetic acid solution, crystallises in colourless, slender needles, m. p. 293°, and yields crystalline *sodium* and *silver* salts; the *iododichloride* could not be obtained in a pure condition.

Ethyl 4-*iododiphenylsulphone*-4′-*carboxylate*, prepared by esterifying the preceding acid, crystallises in slender needles, m. p. 140°; it yields a yellow, crystalline *iododichloride*, $ICl_2 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4 \cdot CO_2Et$ (decomp. 110°), which is converted by aqueous sodium carbonate into *ethyl* 4-*iodosodiphenylsulphone*-4′-*carboxylate*,
$IO \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4 \cdot CO_2Et$,
a pale yellow powder, decomposing at 235°.

4-*Iodophenyl*-2-p-*xylylsulphone*, $C_6H_4I \cdot SO_2 \cdot C_6H_3Me_2$, is obtained in quadrilateral prisms, m. p. 115°, by the interaction of *p*-iodobenzenesulphonyl chloride and *p*-xylene in the presence of aluminium chloride. The *iododichloride*, $ICl_2 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_3Me_2$, forms short, yellow needles (decomp. 138°); 4-*iodosophenyl*-2-p-*xylylsulphone* is a pale yellow powder (decomp. 134°).

2-p-*Xylenesulphonyldiphenyliodinium* (2 : 5-*dimethyldiphenylsulphone*-4′-*phenyliodinium*) *chloride*, $C_6H_3Me_2 \cdot SO_2 \cdot C_6H_4 \cdot IPh \cdot Cl$, is obtained by the action of mercury diphenyl on the preceding iododichloride in chloroform solution; the *platinichloride* (decomp. 182°) and *iodide* (decomp. 135°) are also described. F. B.

4-Amino-1-naphthyl Mercaptan. THEODOR ZINCKE and FRANZ SCHÜTZ (*Ber.*, 1912, **45**, 471—483).—4-*Amino*-1-*naphthyl mercaptan*, $NH_2 \cdot C_{10}H_6 \cdot SH$, m. p. 91—93°, yellow needles, is obtained by reducing 4-acetylamino-1-naphthalenesulphonyl chloride by alcohol, concentrated hydrochloric acid and zinc, and hydrolysing the resulting acetylaminonaphthyl mercaptan by alcohol and hydrochloric acid. The *hydrochloride*, *sulphate*, *acetyl* derivative, m. p. 173°, and *diacetyl* derivative, m. p. 152°, are described. With alcoholic benzaldehyde, it forms the *benzylidene* derivative, $CHPh(S \cdot C_{10}H_6 \cdot N{:}CHPh)_2$, m. p. 68°, yellow powder, in which the benzylidene group attached to the sulphur atoms is hydrolysed by alkalis, and those attached to nitrogen by acids. The *disulphide*, $S_2[C_{10}H_6 \cdot NH_2]_2$, m. p. 168°, is obtained by oxidising the amino-mercaptan with 30% hydrogen peroxide in alcoholic or alkaline solution. It forms a *diacetyl* derivative, m. p. 265°, yellow needles, which is also obtained by the oxidation of the acetylaminonaphthyl mercaptan.

When a suspension of 4-acetylamino-1-naphthyl mercaptan in chloroform or carbon disulphide is treated in a freezing mixture with chlorine (1 mol.), the preceding disulphide is first formed, and then changes to 4-*acetylamino*-1-*chlorothiolnaphthalene*, $NHAc \cdot C_{10}H_6 \cdot SCl$, a yellow

powder, which forms intensely yellow solutions, and is very reactive (compare Abstr., 1911, i, 368), yielding the disulphide with alcohol or formic or acetic acid, and 4-*acetylamino*-1-*acetonylthiolnaphthalene*, $NHAc\cdot C_{10}H_6\cdot S\cdot CH_2\cdot COMe$, m. p. 155—160°, white crystals, with acetone; the last compound is also obtained from chloroacetone and acetylaminonaphthyl mercaptan in dilute sodium hydroxide. 4-*Acetylamino*-1-*bromothiolnaphthalene*, $NHAc\cdot C_{10}H_6\cdot SBr$, is obtained in a similar manner; it can only be isolated in the form of the *hydrobromide*, a yellow powder. An excess of bromine converts 4-acetylamino-1-naphthyl mercaptan in chloroform into 1-*bromo*-4-*acetylaminonaphthalene hydrobromide*, $C_{10}H_6Br\cdot NHAc,HBr$, m. p. 205° (decomp.), straw-yellow needles.

4-*Acetylamino*-1-*naphthyl methyl sulphide*, $NHAc\cdot C_{10}H_6\cdot SMe$, m. p. 193°, yellow needles, is obtained by shaking methyl sulphate and 4-acetylamino-1-naphthyl mercaptan in a slight excess of 10% sodium hydroxide. By hydrolysis with alcohol and concentrated hydrochloric acid, it yields 4-*amino*-1-*naphthyl methyl sulphide hydrochloride*,

$$NH_2\cdot C_{10}H_6\cdot SMe,HCl,$$

white needles, from which the free *base*, $C_{11}H_{11}NS$, m. p. 54°, is obtained. The base is sensitive to oxidising agents, forms solutions with blue fluorescence, reacts with benzaldehyde in alcohol to give 4-*benzylideneamino-a-naphthyl methyl sulphide*, $SMe\cdot C_{10}H_6\cdot N\colon CHPh$, m. p. 56°, yellow needles (which forms an intensely red *salt* with hydrogen chloride in ether), and yields by methylation 4-*dimethylamino*-1-*naphthyl methyl sulphide*, $NMe_2\cdot C_{10}H_6\cdot SMe$, b. p. 199°/16—17 mm. (*hydriodide*, decomp. 171—173°).

4-Acetylamino-1-naphthyl methyl sulphide reacts with bromine in acetic acid to form a *dibromide* (impure), $C_{13}H_{13}ONSBr_2$, m. p. 157° (decomp.), a dark red, crystalline powder, which is converted by boiling glacial acetic acid into the *acetyl* derivative, m. p. 232°, white needles, of 3-*bromo*-4-*amino*-1-*naphthyl methyl sulphide*,

$$NH_2\cdot C_{10}H_5Br\cdot SMe,$$

m. p. 138°, colourless needles. By oxidation in glacial acetic acid with 30% hydrogen peroxide and hydrolysis of the product by alcoholic potassium hydroxide at 100°, 4-acetylamino-1-naphthyl methyl sulphide yields the *sulphoxide*, $NH_2\cdot C_{10}H_6\cdot SO\cdot CH_3$, m. p. 171—172°, colourless crystals (*acetyl* derivative, m. p. 183—184°; a *hydrate*,

$$C_{13}H_{13}O_2NS,\tfrac{1}{2}H_2O,$$

m. p. 109—111°, has also been obtained), the salts of which, unlike those of the parent sulphide, are only slightly hydrolytically dissociated. The sulphoxide reacts with hydrogen bromide in chloroform to form the preceding red dibromide, and its acetyl derivative is oxidised by an excess of hydrogen peroxide to the corresponding *sulphone*, $NHAc\cdot C_{10}H_6\cdot SO_2Me$, m. p. 236°, the hydrolysis of which yields 4-*amino*-1-*naphthylmethylsulphone*, $NH_2\cdot C_{10}H_6\cdot SO_2Me$, m. p. 175° (*hydrochloride*, decomp. about 247°). By warming its solution in acetic acid with a little concentrated hydrochloric acid, 4-amino-1-naphthylmethylsulphoxide is converted into the *hydrochloride* of 3-*chloro*-4-*amino*-1-*naphthyl methyl sulphide*, $NH_2\cdot C_{10}H_5Cl\cdot SMe$, m. p. 71°.

C. S.

Trimethylene [*cyclo*Propane] Derivatives of the Type $\begin{matrix}H_2C\\ |\\ H_2C\end{matrix}\!\!>\!CHX$. LOUIS MICHIELS (*Bull. Acad. roy. Belg.*, 1912, 10—34. Compare Abstr., 1901, i, 581; 1902, i, 525; 1911, i, 62, 459).—A number of ketones, containing the *cyclo*propyl group, have been prepared, and from these the corresponding secondary alcohols have been obtained. Methyl*iso*propylcarbinol has, in particular, been studied with regard to its behaviour towards hydrogen bromide. In the second half of the paper the author considers the physical properties of the *cyclo*propane derivatives as compared with those of the corresponding aliphatic compounds.

cyclo*Propylmethylcarbinol*, $\begin{matrix}H_2C\\ |\\ H_2C\end{matrix}\!\!>\!CH\cdot CHMe\cdot OH$, is obtained by the reduction of *cyclo*propyl methyl ketone with sodium and dry alcohol as a viscous, colourless liquid, b. p. 119—120°, D_4^{20} 0·88045, n_D^{20} 1·42461. With hydrogen chloride it readily yields the corresponding *chloride*, b. p. 105—106°/750 mm., and with hydrogen bromide, in the cold, the *bromide*, a colourless, mobile liquid, b. p. 118—120°/751 mm., D_4^{20} 1·1552. From the bromide by the further action of hydrogen bromide, or from the original carbinol by the action of concentrated hydrobromic acid, a dibromide is obtained, the trimethylene ring being opened, which is probably γ-pentylene dibromide (compare Lipp, Abstr., 1890, 20).

cyclo*Propyl* iso*amyl ketone*, $CHMe_2\cdot[CH_2]_2\cdot CO\cdot CH\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, a colourless liquid with an odour of mint, is obtained by the action of magnesium *iso*amyl bromide on *cyclo*propanecarboxylonitrile, the additive product being decomposed by water and acid. It has b. p. 183—185°/755 mm., D_4^{20} 0·87408, n_D^{20} 1·44064; and yields a *semicarbazone*, m. p. 140—141°. On reduction with sodium and alcohol, cyclo*propyl*iso*amylcarbinol* is formed as a colourless, viscous liquid with a citron-like odour, b. p. 188—189°/766 mm., D_4^{20} 0·8631, n_D^{20} 1·44405.

cyclo*Propyl* iso*hexyl ketone*, $CHMe_2\cdot[CH_2]_3\cdot CO\cdot CH\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, results from the interaction of magnesium *iso*hexyl bromide and ethylene-acetonitrile. It is a colourless, mobile liquid, with an odour of mint, b. p. 200—202°/739 mm., D_4^{20} 0·8631, n_D^{20} 1·44325; on reduction it yields the *carbinol*, a colourless, viscous liquid, with a citron-like odour, b. p. 206—207°/747 mm., D_4^{20} 0·8603, n_D^{20} 1·44345.

cyclo*Propylacetyl*cyclo*propane*, $\begin{matrix}H_2C\\ |\\ H_2C\end{matrix}\!\!>\!CH\cdot CO\cdot CH_2\cdot CH\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, is prepared by the interaction of magnesium *cyclo*propylcarbinyl bromide and *cyclo*propanecarboxylonitrile as a colourless, mobile liquid, b. p. 175—177°/759 mm., D_4^{20} 0·9149, n_D^{20} 1·45787, which yields a *semicarbazone*, m. p. 82—83°. On reduction it gives the corresponding *di*cyclo*propylethanol*, $C_3H_5\cdot CH(OH)\cdot CH_2\cdot C_3H_5$, b. p. 179—180°/770 mm., D_4^{20} 0·9054, n_D^{20} 1·46036. This with hydrogen bromide gives a *bromide*, D_4^{20} 1·535, in which only one of the *cyclo*propane groups has been opened.

The following secondary alcohols were prepared for comparison as regard their physical properties.

iso*Propyl*iso*butylcarbinol*, $CHMe_2\cdot CH(OH)\cdot CH_2\cdot CHMe_2$, is formed by the interaction of magnesium *iso*butyl bromide and *iso*butaldehyde, and subsequent treatment with water and acid. It is a colourless, viscous liquid, smelling of thyme, b. p. 157—158°, D_4^{20} 0·8212, n_D^{20} 1·42461.

iso*Propyl*iso*amylcarbinol*, $CHMe_2\cdot CH(OH)\cdot[CH_2]_2\cdot CHMe_2$, is similarly prepared, and is a colourless, viscous liquid with an odour of balm, b. p. 175°, D_4^{20} 0·8212, n_D^{20} 1·42461.

iso*Propyl*iso*hexylcarbinol* is a similar substance, b. p. 193—194/756 mm., D_4^{20} 0·8152, n_D^{20} 1·43021.

A comparison of the boiling points of the ketones indicates that the loss of two hydrogen atoms accompanying the conversion of $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C$ into $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C$ produces in the case of the methyl-, ethyl-, and *n*-propyl- an increase of 19—20°, and for the *iso*propyl-, *iso*butyl-, and *iso*amyl- an increase of 13—15°. The replacement of a second $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-$ by $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>CH-$ brings about a further rise of 14°. Similar differences are shown by the alcohols.

A study of the densities of the alcohols of the two series shows that, on an average, the density of an alcohol of the *cyclo*propyl series is higher than that of the corresponding aliphatic alcohol by 0·043, and that this value is doubled by the introduction of another *cyclo*propyl group. The molecular refractions of the numerous *cyclo*propane derivatives containing one *cyclo*propyl group show on an average that the value found is higher than that calculated by 0·74 (compare Demjanoff, Abstr., 1907, i, 1032, who gave 0·66). W. G.

Method for Preparing Aromatic Alcohols. GUSTAVE VAVON *Compt. rend.*, 1912, **154**, 359—361).—The reduction of aldehydes to alcohols by the ordinary method, employing sodium amalgam, gives yields not exceeding 50%. A theoretical yield is secured, however, by dissolving the aldehyde in a suitable solvent, adding a few grams of platinum black (prepared by the action of formaldehyde in alkaline solution on platinic chloride), and submitting it to the action of hydrogen under a pressure of about one atmosphere. Successful application to a number of aromatic aldehydes of varied types shows that the reaction is a general one. W. O. W.

Betulin. I. K. TRAUBENBERG (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 132—138).—The author's investigations on betulin (compare Hausmann, Abstr., 1877, i, 94; Franchimont and Wigman, Abstr., 1879, 468), which include the determination of the molecular weight in boiling chloroform by Landsberger's method and in freezing benzene and also the preparation and analysis of the diacetyl and dibenzoyl derivatives, indicate that betulin has the formula

$$C_{24}H_{38}(OH)_2,$$

and that it belongs, together with onocol, arnidiol, and faradiol to a group of dextrorotatory dihydric phytosterols.

Betulin, m. p. 251°, $[\alpha]_D$ +15·68°, gives a number of colour reactions similar to those for cholesterol. Its diacetyl compound has $[\alpha]_D$ +14·26°, and its *dibenzoyl* derivative, $C_{24}H_{38}O_2Bz_2$, has m. p. 145—147°. When oxidised by means of alkaline permanganate, betulin yields acetic acid and a solid acid which was not investigated, whilst with chromic acid it gives a *ketone*, $C_{24}H_{38}O_2$, crystallising in prisms, m. p. 177°, and yielding a *phenylhydrazone*, $C_{24}H_{38}O{\cdot}N_2HPh$, m. p. 130°. T. H. P.

Preparation and Estimation of Tyrosine and Glutamic Acid. Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1912, **77**, 75—76).—Tyrosine can be prepared from silk by the simple method of hydrolysing with hydrochloric acid; the acid is removed by evaporation, and then by the addition of sodium hydroxide; tyrosine then crystallises out from the hot aqueous solution. The yield, however, is not quantitative, and the mother liquor is not available for the separation of other amino-acids. These two disadvantages can be overcome in the following way. After hydrolysing with hydrochloric acid, the product is evaporated under reduced pressure to dryness; the residue is dissolved in water, and a stream of ammonia passed through the solution. It is then again evaporated to dryness, and the residue treated with cold water; tyrosine is left undissolved, or the whole residue may be boiled with water and animal charcoal; from the filtrate pure tyrosine crystallises out quantitatively. The mother liquor is again evaporated to dryness, and the residue treated by the ester method for the other mono-amino-acids. The method serves for the estimation of tyrosine, etc., in like products of hydrolysis.

Glutamic acid may be prepared from its hydrochloride by passing ammonia through the solution and then evaporating to dryness. The deposit is dissolved in hot water and recrystallised; the main amount of glutamic acid can be separated by fractional crystallisation, and the remainder can be obtained by precipitation with alcohol.

W. D. H.

[Di-iodotyrosine.] A Correction. Adolf Oswald (*Zeitsch. physiol. Chem.*, 1912, **76**, 499—500).—Polemical (compare Abderhalden and Hirsch, Abstr., 1911, ii, 1119). E. F. A.

Melting Point of 3:5-Di-iodotyrosine. Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1912, **77**, 183—184).—Polemical. A reply to Oswald (preceding abstract). W. D. H.

Action of Hydrogen Sulphide on Imino-ethers. II. Formation of Thion Esters and Acids. Motooki Matsui (*Mem. Koll. Sci. Eng. Kyōtō*, 1912, **3**, 247—255. Compare Abstr., 1909, i, 463).—When hydrogen sulphide is passed into an ethereal solution of an imino-ether, a thion ester is produced, which ultimately reacts with the liberated ammonia with the formation of a thioamide. In alcoholic solution, however, ammonia decomposes thion esters with the formation of imino-ethers, hydroxylamine having a similar action.

By saponifying thion esters with cold alkali, it has been found possible to prepare the corresponding acids. Thion-fatty acids are volatile, pale yellow liquids, having a strong penetrating odour resembling that of acetic acid and a very acidic reaction; thion-aromatic acids are yellow, solid substances of characteristic odour. All are unstable, decomposing even in ethereal solution in the course of a few days. They show a marked difference from ordinary mono-carboxylic acids, in that their silver and lead salts remain in the ethereal layer when an ethereal solution of the acid is shaken with an aqueous solution of silver nitrate or lead acetate. Silver salts of thion-fatty acids are very unstable, readily changing into silver sulphide, whilst those of the aromatic acids are comparatively stable at the ordinary temperature.

Ethyl thionbenzoate (*loc. cit.*) is a yellow liquid of b. p. 181°/360 mm. When its alcoholic solution is treated with ammonia, it yields ethyl iminobenzoate, whilst in ethereal solution, thiobenzamide is formed. Hydroxylamine reacts with an alcoholic solution of the ester, yielding a mixture of α- and β-ethylbenzhydroxamic acids.

Methyl thionbenzoate resembles the ethyl ester. It has b. p. 195—197°/320 mm.

Methyl thionacetate has b. p. 85—90°; *methyl thionpropionate* has b. p. 110—115°.

*Ethyl thion-*p*-toluate* is a yellow oil, b. p. 205—207°/260 mm., m. p. about 1°.

Thionbenzoic acid was prepared by hydrolysing ethyl thion-benzoate with cold sodium hydroxide. Its *silver*, *lead*, and *barium* salts were examined. *Thion-*p*-toluic acid* was similarly prepared, but in quantity insufficient for complete characterisation. *Thionacetic acid* could not be obtained free from ether, but has b. p. about 37°. The similar *thionpropionic acid* was also prepared, and its *lead* salt was investigated. H. W.

Terpenes and Ethereal Oils. CVIII. OTTO WALLACH (*Annalen*, 1912, 388, 49—62).—Semmler's method of preparing tanacetophorone by the distillation of salts of tanacetonedicarboxylic acid is unsatisfactory with regard to yield and purity of product. A very convenient process is the following: *Methyl α-tanacetonedi-carboxylate*, $CH_2<\begin{matrix}CH\cdot CO_2Me\\ |\\ CPr^{\beta}\cdot CH_2\cdot CO_2Me\end{matrix}$, b. p. 244—247° or 126—127°/13 mm., D^{20} 1·0535, n_D^{20} 1·4506, $[\alpha]_D$ 142·5°, obtained from the acid, methyl alcohol, and hydrogen chloride, forms with sodium in methyl alcohol a yellow, crystalline *compound*, $C_{10}H_{13}O_3Na,H_2O$, which develops a violet coloration with ferric chloride, yields impure tanacetophoronesemicarbazone with aqueous semicarbazide hydro-chloride, and is converted into tanacetophorone by the successive operations of boiling its aqueous solution, acidifying with sulphuric acid, and distillation with steam. The transformations in the preparation of the ketone are probably as follows. Methyl α-tan-acetonedicarboxylate ⟶ methyl β-tanacetonedicarboxylate,

$$CH_2<\begin{matrix}CH_2\cdot CO_2Me\\ CPr^{\beta}{:}CH\cdot CO_2Me\end{matrix} \longrightarrow$$

methyl 1-*iso*propyl-Δ'-*cyclo*penten-3-one-2-carboxylate,

$$CH_2<\begin{matrix}CH_2-CO\\ CPr^{\beta}:C\cdot CO_2Me\end{matrix}, \longrightarrow$$

sodium derivative, $CH_2<\begin{matrix}CH{=}C\cdot ONa\\ CPr^{\beta}:C\cdot CO_2Me\end{matrix}$, $\longrightarrow$ tanacetophorone,

$$CH_2<\begin{matrix}CH{=}C\cdot OH\\ CPr^{\beta}:CH\end{matrix}, \rightleftarrows CH_2<\begin{matrix}CH_2-CO\\ CPr^{\beta}:CH\end{matrix}.$$

The preceding constitution of the sodium compound is supported by the fact that the substance, dissolved in water saturated with carbon dioxide, is converted into dihydrotanacetophorone (1-*iso*-propyl*cyclo*pentan-3-one) by treatment with hydrogen and colloidal palladium, and subsequent acidification and distillation with steam.

[With FREDERIK CHALLENGER].—1-*iso*Propyl*cyclo*pentan-3-one, b. p. 188—189°, D^{21} 0·9000, n_D^{21} 1·4428 (compare Abstr., 1911, i, 472), forms a *dibenzylidene* derivative, m. p. 134—135°, yellow needles, and reacts with magnesium methyl iodide to yield ultimately i-1-*methyl*-3-iso*propyl*cyclo*pentan*-1-*ol*, $C_9H_{18}O$, b. p. 185—186°, m. p. 43—44°, which apparently is the inactive modification of the tertiary alcohol obtained by the action of nitrous acid on fenchylamine (Abstr., 1911, i, 311); by dehydration with oxalic acid, it yields a hydrocarbon, C_9H_{16}, b. p. 142—144°, D^{20} 0·7970, n_D^{20} 1·4418, which is almost identical in chemical and physical properties with that described previously (*loc. cit.*). C. S.

The Ethyl Ester of Naphthalic Acid. WILHELM WISLICENUS and OTTO PENNDORF (*Ber.*, 1912, 45, 410—411).—Naphthalic acid cannot be esterified directly. The diethyl ester described recently by Errera (Abstr., 1911, i, 465) had already been prepared by the authors by the action of ethyl iodide on silver naphthalate; it has m. p. 59—60° and b. p. 238—239°/19 mm.; the solution in strong sulphuric acid shows a blue fluorescence. D. F. T.

Methylamino- and Other Derivatives of Terephthalic Acid. RUDOLF WEGSCHEIDER, FRANZ FALTIS, SIEGMUND BLACK, and OSKAR HUPPERT (*Monatsh.*, 1912, 93, 141—168).—The object of the investigation was a convenient method for the preparation of meth l- and dimethyl-aminoterephthalic acids.

Aminoterephthalic acid was obtained by successive nitration and reduction of terephthalic acid; the corresponding methyl ester was obtained by esterification of the acid, and also by the reduction of the methyl ester of nitroterephthalic acid; the last-named substance can be prepared by careful nitration of the methyl terephthalate, as well as by esterification of nitroterephthalic acid.

The methyl ester of acetylaminoterephthalic acid (compare Cahn-Speyer, Abstr., 1907, i, 849) is obtained by simple acetylation with acetic anhydride; the alcoholic mother liquors from the recrystallisation of this substance contain *methyl diacetylaminoterephthalate*, which is also obtainable by the further acetylation of the monoacetyl compound; the crystals of the substance, m. p. 74—76°, belong to the triclinic system [$a:b:c=0·5240:1:0·7912$; $\alpha=91°12$, $\beta=85°22'$, $\gamma=96°19'$]; water hydrolyses the substance into the monoacetyl compound.

Methylaminoterephthalic acid is best prepared by the action of methyl sulphate on aminoterephthalic acid in the presence of barium carbonate; it has m. p. 273·5—274·5° (corr.) (compare Cahn-Speyer, *loc. cit.*); the solutions show a blue fluorescence. When the methyl-alcoholic solution is treated with hydrogen chloride at room temperature, 4-*methyl* 1-*hydrogen* 2-*methylaminoterephthalate* separates, m. p. 186·5—187° (corr.). The corresponding *dimethyl* ester was also obtained by esterification as an impure, dark yellow solid, m. p. 86·5—90°

Acetylmethylaminoterephthalic acid was not obtainable by methylating the acetylamino-acid with methyl sulphate, but was successfully prepared by acetylating the methylamino-acid; it crystallises in crusts, the m. p. of which, 216—216·5°, is much below that given by Cahn-Speyer; it is colourless and does not give fluorescent solutions. The acetyl group is removed by the action of dilute potassium hydroxide solution.

Methyl acetylmethylaminoterephthalate, obtained by the action of potassium and methyl iodide on a benzene solution of the methyl acetylaminoterephthalate, has m. p. 78—80°; the acetyl group is hydrolysed off by heating with water.

Dimethylaminoterephthalic acid is best prepared by energetic methylation of aminoterephthalic acid with methyl sulphate in the presence of barium carbonate; it is a white, crystalline solid, m. p. 281° (corr.; decomp.). The *dimethyl* ester, obtained from the acid by esterification in the usual way, crystallises in needles belonging to the triclinic system [$a:b:c = 0·7920:1:0·8327$; $\alpha = 82°21'$, $\beta = 94°14'$, $\gamma = 104°50'$], m. p. 68—69°. D. F. T.

Reduction of Acids with Several Double Bonds by Paal's Method. WALTHER BORSCHE (*Ber.*, 1912, **45**, 620—625).—Unsaturated acids when shaken with hydrogen and colloidal platinum are readily converted into the saturated substances.

Cinnamylideneacetic acid, $CHPh\colon CH\cdot CH\colon CH\cdot CO_2H$, yields phenylvaleric acid. Cinnamylidenemalonic acid, $CHPh\colon CH\cdot CH\colon C(CO_2H)_2$, gives *ω-phenyl-*n*-propylmalonic acid*, crystallising in colourless platelets, m. p. 98°. When heated, carbon dioxide is eliminated and δ-phenylvaleric acid obtained; this is the most convenient method for its preparation.

Methyl ω-phenylpropylmalonate, formed by reduction of methyl cinnamylidenemalonate, is a colourless oil, b. p. 183—184°/10 mm.

α-Cyano-δ-phenylvaleric acid, prepared by reduction of α-cyanocinnamylideneacetic acid, is obtained as an oil, which on distillation is converted into δ-phenylvaleronitrile.

The *ethyl* ester of α-cyano-δ-phenylvaleric acid is a colourless oil, b. p. 192—193°/11 mm.

αδ-Diphenylvaleric acid, $CH_2Ph\cdot CH_2\cdot CH_2\cdot CHPh\cdot CO_2H$, from α-phenylcinnamylideneacetic acid, crystallises in bunches of colourless needles, m. p. 80—81° (compare Rupe and Liechtenhan, Abstr., 1909, i, 927).

αδ-Diphenylvaleronitrile from cinnamylidenephenylacetonitrile forms large, transparent crystals with lustrous faces, m. p. 79°; it distils without decomposition. E. F. A.

Syntheses in the Fatty Aromatic Series. III. [Amino-acids, Nitro-compounds, Aldehydes.] JULIUS VON BRAUN and O. KRUBER (*Ber.*, 1912, **45**, 384—402. Compare Abstr., 1911, i, 968; 1910, i, 843).—The authors have attempted in several ways to prepare the series of aldehydes corresponding with the series of alcohols already described in the earlier papers; the most satisfactory source for the aldehydes proves to be the primary nitro-compounds.

Various phenyl substituted amino-acids were obtained by applying the malonic ester synthesis as described by the series of changes:

$$CH_2Ph\cdot[CH_2]_x\cdot Br \longrightarrow CH_2Ph\cdot[CH_2]_x\cdot CH\cdot(CO_2H)_2 \longrightarrow$$
$$CH_2Ph\cdot[CH_2]_x\cdot CHBr\cdot CO_2H \longrightarrow CH_2Ph\cdot[CH_2]_x\cdot CH(NH_2)\cdot CO_2H.$$

δ-Phenylpropylmalonic acid, $CH_2Ph\cdot[CH_2]_2\cdot CH(CO_2H)_2$, m. p. 94°, is obtained by hydrolysis of the *ethyl* ester, a colourless oil, b. p. 189—194°/13 mm. On distillation under reduced pressure, it loses carbon dioxide with the formation of δ-phenylvaleric acid. Bromination in ethereal solution yields α-bromo-δ-phenylpropylmalonic acid, m. p. 135—136°; this when heated above its m. p. loses carbon dioxide and forms *α-bromo-δ-phenylvaleric acid*,

$$CH_2Ph\cdot[CH_2]_2\cdot CHBr\cdot CO_2H,$$

m. p. 85°, b. p. 195—210°/15 mm.; the same substance is obtained in a less pure condition by brominating δ-phenylvaleric acid. If the bromo-acid is heated with a concentrated aqueous solution of ammonia, there is obtained *α-amino-δ-phenylvaleric acid*, m. p. 203—206°; the *copper* salt was prepared, also the *β-naphthalenesulphonyl* derivative, m. p. 83°.

ε-Phenylbutylmalonic acid, $CH_2Ph\cdot[CH_2]_3\cdot CH(CO_2H)_2$, needles, m. p. 111°, is obtained by hydrolysis of the *ethyl* ester, b. p. 215—218°/11 mm.; bromination gives *α-bromo-ε-phenylbutylmalonic acid*, m. p. 123—124° (decomp.), which on heating yields *α-bromo-ε-phenylhexoic acid*, a yellow oil, b. p. 210—230°/12 mm., which would not crystallise; the preparation of this last substance by bromination of ε-phenylhexoic acid is again unsatisfactory. When heated with aqueous solution of ammonia, the bromo-acid is converted into *α-amino-ε-phenylhexoic acid*, white, leafy crystals, m. p. 237—242° (decomp.); the *copper* salt and the *β-naphthalenesulphonyl* derivative, m. p. 112—113°, were prepared.

The above amino-acids failed to supply the desired easy passage to the required aldehydes.

Phenylbutyronitrile, $CH_2Ph\cdot[CH_2]_2\cdot CN$, when treated in alcoholic solution with dry hydrogen chloride yields the *hydrochloride* of *phenylbutyrimido-ether*, $CH_2Ph\cdot[CH_2]_2\cdot C(:NH)\cdot OEt,HCl$, which by the action of aniline in alcoholic solution is converted into the corresponding *diphenylamidine* compound, $CH_2Ph\cdot[CH_2]_2\cdot C(:NPh)\cdot NHPh$, a white, crystalline solid, m. p. 81—82°. Reduction of this compound by sodium and alcohol yields a non-volatile, viscous oil, probably *di-δ-anilino-α-phenylbutane*, $CH_2Ph\cdot[CH_2]_2\cdot CH(NHPh)_2$, which on hydrolysis yields only a few drops of δ-phenylbutaldehyde (compare Merling, Abstr., 1908, i, 653).

If phenylpropyl bromide is allowed to react with magnesium and then with ethyl orthoformate, the expected *phenylbutaldehyde diethyl acetal*, $CH_2Ph\cdot[CH_2]_2\cdot CH(OEt)_2$, is obtained; it is, however,

much decomposed during distillation (b. p. about 200°/20 mm.); hydrolysis gives a very poor yield of the aldehyde. Phenylbutyl bromide, magnesium and ethyl orthoformate yield no better result (compare Tschitschibabin, Abstr., 1904, i, 221; Bodroux, Abstr., 1904, i, 421).

The reaction of magnesium phenylpropyl bromide and formomethylanilide gives no trace of phenylbutaldehyde (compare Houben and Döscher, Abstr., 1908, i, 27), whilst the action of sodium hypochlorite on a hot aqueous solution of α-amino-δ-phenylvaleric acid or α-amino-ε-phenylhexoic acid yields small quantities of δ-phenylbutaldehyde and ε-phenylvaleraldehyde respectively (compare Langheld, Abstr., 1909, i, 138).

The desired aldehydes were satisfactorily obtained by starting with the primary nitro-compounds, which by reduction are convertible into the aldoximes (Konowaloff, Abstr., 1899, i, 733).

The interaction of γ-phenylpropyl iodide and silver nitrite produced *γ-phenylpropyl nitrite*, b. p. 115—125°/14 mm., and *γ-nitro-α-phenylpropane*, a colourless, inodorous oil, b. p. 147—148°/11 mm.; the latter on treatment with bromine in aqueous solution gives oily *di-γ-bromo-γ-nitro-α-phenylpropane*, $CH_2Ph\cdot CH_2\colon CBr_2\cdot NO_2$, whilst with a diazonium salt it yields *α-nitro-γ-phenylpropaldehydephenylhydrazone*, small, red needle crystals, m. p. 133—134°; the *α-phenylpropanenitrolic acid* has m. p. 75°. If the *sodium* compound of nitrophenylpropane is reduced in aqueous solution by stannous chloride, there is obtained *γ-phenylpropaldoxime*, m. p. 93—94°; this on hydrolysis yields γ-phenylpropaldehyde, $Ph\cdot[CH_2]_2\cdot CHO$, b. p. 110—113°/16 mm. (compare Fischer and Hoffa, Abstr., 1898, i, 659); the *diphenylmethanedimethyldihydrazone*, $CH_2[C_6H_4\cdot NMe\cdot N\colon CH\cdot CH_2\cdot CH_2Ph]_2$, has m. p. 99—100°.

δ-Nitro-α-phenylbutane (together with *δ-phenylbutyl nitrite*, b. p. 125—130°/15 mm.) is obtained similarly to the corresponding propane derivative as a colourless oil of feeble odour, b. p. 160—165°/15 mm.; reduction of the sodium salt in aqueous solution and subsequent hydrolysis yields *δ-phenylbutaldehyde*, $CH_2Ph\cdot[CH_2]_2\cdot CHO$, b. p. 129—131°/17 mm.; the *semicarbazone* has m. p. 104—105°; the *phenylhydrazone* is an oil; the *diphenylmethanedimethyldihydrazone* crystallises very slowly; the *methyl acetal* has b. p. 121—124°/9 mm.

ε-Nitro-α-phenylpentane is a colourless, inodorous liquid, b. p. 161—166°/9 mm., whilst the isomeric *ε-phenylamyl nitrite* has b. p. 130—135°/10 mm. The *dibromo*-derivative of the phenylnitropentane is a yellow oil; the *nitrolic acid* derivative and the product of coupling with a diazonium salt also show little tendency to crystallise. Reduction and subsequent hydrolysis of the nitro-compound yield *ε-phenyl-*n*-valeraldehyde*, $CH_2Ph\cdot[CH_2]_3\cdot CHO$, as an oil, b. p. 129—131°/10 mm., strongly resembling citral in odour; the *methyl acetal*, b. p. 136—139°/11 mm., has only a faint ethereal odour. The *oxime*, *semicarbazone*, *phenylhydrazone*, and *diphenylmethanedimethyldihydrazone* are oily; the p-*nitrophenylhydrazone* slowly gives a solid, m. p. 82—84°.

ζ-Nitro-α-phenylhexane has b. p. 174—178°/11 mm., whilst the isomeric *ζ-phenylhexyl nitrite* has b. p. 143—148°/11 mm. The nitro-

compound is easily converted into *ζ-phenylhexaldehyde*,

$$CH_2Ph\cdot[CH_2]_4\cdot CHO,$$

b. p. 141—144°/9 mm., of feeble and not unpleasant odour; the substance offers considerable resistance to satisfactory analysis by combustion.

η-Nitro-α-phenylheptane has b. p. 182—186°/10 mm., and the isomeric *η-phenylheptyl nitrite*, b. p. 164—166°/13 mm. The nitro-compound is convertible by the general process into *η-phenylheptaldehyde*,

$$CH_2Ph\cdot[CH_2]_5\cdot CHO,$$

b. p. 155—159°/9 mm., which like the lower aldehyde offers resistance to satisfactory combustion; it has a feeble odour. The p-*nitrophenylhydrazone* is a brown powder, m. p. 68—70°.

The above series of aldehydes, with the striking exception of δ-phenylvaleraldehyde, show a gradual weakening of the odour with increase in the length of the carbon chain; this is in marked contrast to the oscillatory effect observed with the corresponding series of alcohols. D. F. T.

Combination of Phenolcarboxylic Acids. FERDINAND MAUTHNER (*J. pr. Chem.*, 1912, [ii], **85**, 308—314).—An isomeride of the previously-described 3 : 4 : 5 : 2′ : 6′-pentamethyl ether of methyl digallate (Abstr., 1911, i, 725) has been synthesised by condensing 3 : 4 : 5-trimethoxybenzoyl chloride with methyl 5-hydroxy-3 : 4-dimethoxybenzoate. The condensation was effected by shaking the ester in aqueous sodium hydroxide solution with an ethereal solution of the acid chloride.

Methyl 5-(3′ : 4′ : 5′)-*trimethoxybenzoyloxy*-3 : 4-*dimethoxybenzoate*, $C_6H_2(OMe)_3\cdot CO_2\cdot C_6H_2(OMe)_2\cdot CO_2Me$, thus obtained crystallises in colourless needles, m. p. 127—128°, and is the completely methylated derivative of the digallic acid isolated by Nierenstein (Abstr., 1910, i, 265) from tannin.

The following compounds were prepared in a similar manner:

Methyl p-3 : 4 : 5-*trimethoxybenzoyloxybenzoate*, $C_{18}H_{18}O_7$, obtained from 3 : 4 : 5-trimethoxybenzoyl chloride and methyl *p*-hydroxybenzoate, has m. p. 109—110°.

Methyl 4-(3′ : 4′ : 5′)-*trimethoxybenzoyloxy*-3-*methoxybenzoate*, $C_{19}H_{20}O_8$, prepared from 3 : 4 : 5-trimethoxybenzoyl chloride and methyl vanillate, forms colourless needles, m. p. 131—132°.

Methyl p-4-*methoxybenzoyloxybenzoate*, $C_{16}H_{14}O_5$, obtained from anisoyl chloride and methyl *p*-hydroxybenzoate, crystallises in colourless needles, m. p. 146—147°.

Methyl 4-*veratroyloxy*-3-*methoxybenzoate*, $C_{17}H_{16}O_6$, from veratroyl chloride and methyl vanillate, has m. p. 128—129°.

Methyl p-*veratroyloxybenzoate*, $C_{18}H_{18}O_7$, forms colourless needles, m. p. 148—149°. F. B.

Mechanism of Cannizzaro's Reaction. VETCHESLÁV E. TISTSHENKO, I. F. VELTSA, and I. L. RABTSEVITSCH-ZUBKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 138—151).—According to Claisen (Abstr., 1887, 574), when a sodium alkyloxide is heated in alcoholic solution

with benzaldehyde, a voluminous, white precipitate is formed, which is decomposed by water into benzyl alcohol and sodium benzoate, or by acetic acid into benzyl benzoate and alkyl benzoate; he regarded this precipitate as an intermediate compound formed according to the equation:

$$2Ph{\cdot}CHO + R{\cdot}ONa = CPh\begin{cases} O{\cdot}CH_2Ph \\ OR \\ ONa \end{cases}.$$

The authors have investigated this reaction under various conditions, and in all cases find the precipitate formed to consist simply of sodium benzoate. As has been previously asserted (Abstr., 1907, i, 282), Claisen's explanation must be abandoned. T. H. P.

The Action of Solutions of Ethoxides on *m*-Nitrobenzylidene Chloride. ALFRED KLIEGL (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 226—228. Compare Kliegl and Haas, Abstr,, 1911, i, 433).—*m*-Nitrobenzylidene chloride yields with solutions of ethoxides the acetal of *m*-nitrobenzaldehyde, but this is accompanied into two compounds of the same composition and molecular weight, but higher boiling point. They are unchanged by boiling with dilute sulphuric acid. Heating with hydrogen bromide in acetic acid forms bromo-derivatives, from which the alcohols may be obtained. Oxidation with permanganate then yields compounds which are identified as ethers of 5-nitrosalicylic acid and 3-nitro-4-hydroxybenzoic acid respectively. The original compounds are therefore derived from *m*-nitrobenzylidene chloride by the wandering of a chlorine atom into the nucleus, followed by the replacement of chlorine by alkyloxy-groups.

C. H. D.

Action of Benzaldehyde on Polyhydric Alcohols Derived from Sugars. JEAN MEUNIER (*Ann. Chim. Phys.*, 1912, [viii], **25**, 286—288).—The author points out that the condensation of polyhydric alcohols with benzaldehyde to form acetals was first noticed by him in 1888 (Abstr., 1888, 950, 1265; 1889, 233, 479; 1890, 730), and is wrongly attributed to E. Fischer in a recent paper (*Ann. Chim. Phys.*, 1911, [viii], **24**, 398).

The sorbitol derivative described already (Abstr., 1889, 479) may be prepared by mixing the components at 0°, concentrating to a syrup of 33°Bé., and adding 60% sulphuric acid. The crystalline product which deposits is separated and washed, and can be used for the production of pure sorbitol by hydrolysing with 0·002% sulphuric acid at 100° and distilling under reduced pressure, when the benzaldehyde passes over in the steam, leaving pure sorbitol. T. A. H.

Aromatic Amino-ketones. FRANZ KUNCKELL (*Ber. deut. pharm. Ges.*, 1912, **22**, 103—114. Compare Abstr., 1900, i, 663; 1911, i, 990).—The methods described in the preceding paper of this series (*loc. cit.*) have been applied to *p*-acetotoluidide and the products obtained are described.

[With CARL BLUMENREUTER.]—ω-Chloro-2-acetylamino-5-methylaceto

phenone, $CH_2Cl\cdot CO\cdot C_6H_3Me\cdot NHAc$, already described (Abstr., 1900, i, 663) reacts with potassium acetate to form an *acetate*,

$$OAc\cdot CH_2\cdot CO\cdot C_6H_3Me\cdot NHAc,$$

m. p. 94°, and with bromine to give *ω-chloro-ω-bromo-2-acetylamino-5-methylacetophenone*, m. p. 138°, and this on hydrolysis with 20% hydrochloric acid loses 1 mol. of acetic acid and forms the corresponding *amine*, m. p. 123°, bright yellow needles. On treatment with warm dilute sodium hydroxide solution, the chlorobromo-ketone yields dimethylindigotin.

On nitration of ω-chloro-2-acetylamino-5-methylacetophenone, one nitro-group enters, probably in the unoccupied *o*-position to the acetylamino-group; the *nitro*-derivative, m. p. 167°, forms glancing, yellow needles, and on treatment with alkalis does not yield a substituted indigotin. With aniline the chlorine atom in the parent substance is replaced, and the *substance*, $NHPh\cdot CH_2\cdot CO\cdot C_6H_3Me\cdot NHAc$, m. p. 146°, formed, crystallising in yellow needles.

ω-Chloro-3-acetylamino-6-methylacetophenone, formed along with its isomeride (see above), yields (1) on bromination *ω-chloro-ω-bromo-3-acetylamino-6-methylacetophenone*, m. p. 112°, colourless leaflets, from which the corresponding *amine*, m. p. 88°, yellow needles, is produced on hydrolysis; (2) by nitration, indefinite products; (3) by treatment with aniline, the corresponding *aniline* derivative,

$$NHPh\cdot CH_2\cdot CO\cdot C_6H_3Me\cdot NHAc,$$

m. p. 184°, colourless needles; (4) with potassium acetate in dilute alcohol, the corresponding *acetate*, $OAc\cdot CH_2\cdot CO\cdot C_6H_3Me\cdot NHAc$, m. p. 94°, hard, colourless needles.

m-Bromo-*p*-acetotoluidide reacts with chloroacetyl chloride to form *ω-chloro-*2(or 4)*-bromo-3-acetylamino-6-methylacetophenone*, m. p. 134°, glancing, colourless leaflets, which on hydrolysis yields the corresponding *amine*, m. p. 116°, glancing, yellow needles, giving a *hydrochloride*, m. p. 206° (decomp.), colourless needles. T. A. H.

Interesting Decomposition of Some Oximes. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 83—84).—Benzophenoneoxime decomposes at about 180° according to the equation:

$$3CPh_2{:}N\cdot OH = 3COPh_2 + N_2 + NH_3.$$

If it is supposed that the nitrogen and ammonia are produced according to the equation: $3NH = N_2 + NH_3$, the Beckmann rearrangement becomes explicable on the hypothesis that a similar decomposition of the oxime first occurs, but the NH: group takes up another position in the molecule instead of giving rise to nitrogen and ammonia. Analogous decompositions are those of some nitronic acids (Nef), and of phthalylphenylhydrazide (compare Chattaway, Cumming, and Wilsdon, Trans., 1911, **99**, 1950). R. V. S.

Preparation of αε-Diphenyl-ββδδ-tetramethylpentan-γ-one and of α-Phenyl-ββδδ-tetramethylpentan-γ-one, Derivatives of Dibenzylacetone (αε-Diphenylpentan-γ-one) and of α-Phenylpentan-γ-one. ALBIN HALLER (*Compt. rend.*, 1912, **154**, 555—559).—αε-Diphenylpentanone was repeatedly methylated by means of sodamide and methyl iodide. The final product was *αε-diphenyl-*

ββδδ-tetramethylpentan-γ-one, $CH_2Ph\cdot CMe_2\cdot CO\cdot CMe_2\cdot CH_2Ph$, an oily liquid, b. p. 203—208°/10 mm.; when heated with sodamide it undergoes scission in the normal way. The same method of methylation applied to α-phenylpentan-γ-one leads to the formation of *α-phenyl-ββδδ-tetramethylpentan-γ-one*, $CH_2Ph\cdot CMe_2\cdot CO\cdot CMe_3$, b. p. 139—144°/16 mm. The new tetra-alkyl ketones do not react with hydroxylamine, semicarbazide, or phenylhydrazine. W. O. W.

Dihalogenoindones. HUGO SIMONIS and CURT KIRSCHTEN (*Ber.*, 1912, **45**, 567—579).—From his investigations on the condensation of 2:3-dibromo-1-indone and dibromo-derivatives of quinones with ethyl malonate and other substances containing a reactive methylene group, Liebermann (Abstr., 1899, i, 219, 373, 522; 1900, i, 310, 666) has drawn the conclusion that the mobility of the halogen atoms in these compounds is due to the group $CBr\colon CBr\cdot CO$ being contained in a closed ring.

It is now shown that the mobility is connected with the presence of the carbonyl group, for compounds in which this group is lacking have their halogen atoms firmly attached; thus, 2:3-dibromo-1-methyl-1-indenol, $C_6H_4<\begin{matrix}\text{——CBr}\\ \text{CMe(OH)}\end{matrix}>CBr$, does not condense with substances containing a reactive methylene group, and undergoes no change on treatment with potassium iodide or benzylamine.

The reaction between magnesium methyl bromide and 2:3-dibromo-1-indone yields 3-bromo-2-iodo-1-indone, which crystallises in brown prisms, subliming above 80° with partial decomposition, m. p. 158° (compare Roser and Haselhoff, Abstr., 1888, 1317), and 2:3-*dibromo-1-methyl-1-indenol*. The latter compound crystallises in white platelets, m. p. 126·5—127°, combines with bromine to form 2:2:3:3-*dibromo-1-methyl-1-hydrindenol*, $C_6H_4<\begin{matrix}\text{—}CBr_2\text{—}\\ \text{CMe(OH)}\end{matrix}>CBr_2$, and is converted by hydrogen bromide in glacial acetic acid solution into 1:2:3-*tribromo-1-methylindene*, $C_6H_4<\begin{matrix}\text{—CBr}\\ \text{CMeBr}\end{matrix}>CBr$, pale yellow prisms, m. p. 78°; the *acetyl* derivative crystallises in lustrous, white needles, m. p. 82°.

2-*Iodo-3-benzylamino-1-indone*, $CO<\begin{matrix}C_6H_4\\ \text{—CI}\end{matrix}>C\cdot NH\cdot C_7H_7$, prepared either by heating 3-bromo-2-iodo-1-indone with benzylamine in alcoholic solution or from potassium iodide and 2-bromo-3-benzylamino-1-indone (Schlossberg, Abstr., 1900, i, 665), crystallises in long, red needles, m. p. 138° (decomp.). The action of ethylamine and aniline on 3-bromo-2-iodo-1-indone yields orange-red compounds of a similar constitution.

Attempts to prepare 2-bromo-3-benzylamino-1-indone by brominating 3-benzylamino-1-indone (Schlossberg, *loc. cit.*) resulted in the removal of the benzylamino-group and the formation of a *dibromo-1-indone*, $C_6H_3Br<\begin{matrix}CBr\\ \text{CO-}\end{matrix}>CH$, which crystallises in reddish-brown needles, m. p. 177°, and contains one of the bromine atoms in the benzene nucleus.

3-*Bromo-2-iodo-1-indoneoxime*, C_9H_5ONBrI, exists in two stereoisomeric forms, one crystallising in yellow needles, m. p. 206°, the

other in yellow, quadratic plates, m. p. 195—197°; the p-*nitrophenylhydrazone* forms brownish-red, microscopic needles, m. p. 212—214°.

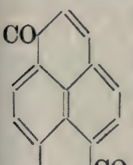
On treatment with bromine, 3-bromo-2-iodo-1-indone is converted into 2 : 2 : 3 : 3-tetrabromohydrindene (Roser and Haselhoff, *loc. cit.*); with magnesium methyl iodide it forms 3-*bromo*-2-*iodo*-1-*methyl*-1-*indenol*, $C_6H_4{<}\begin{matrix}CBr\\CMe(OH)\end{matrix}{>}CI$, which crystallises in almost white leaflets, m. p. 137°.

2 : 3-*Dibromo*-1-*ethyl*-1-*indenol*, $C_{11}H_{10}OBr_2$, prepared from magnesium ethyl bromide and 2 : 3-dibromo-1-indone, crystallises in colourless prisms, belonging to the rhombic system, m. p. 77—78°, and yields an *acetyl* derivative, m. p. 91°.

2 : 3-*Dibromo*-1-*phenyl*-1-*indenol* could not be obtained in a pure condition, and was therefore characterised by means of its *acetyl* derivative, $C_{17}H_{12}O_2Br_2$, which forms pale grey, prismatic needles, m. p. 138—140°.

F. B.

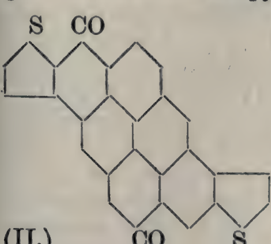
Catalytic Elimination of Hydrogen from Aromatic Nuclei and the Synthesis of Condensed Systems by means of Aluminium Chloride. ROLAND SCHOLL and CHRISTIAN SEER (*Monatsh.*, 1912, 33, 1—8).—When aromatic compounds are heated with anhydrous aluminium chloride at from 80° to 140°, hydrogen is eliminated and a new ring formed. Previous examples of this are the conversion of naphthalene and α-dinaphthyl into perylene (Scholl, Seer, and Weitzenböch, Abstr., 1910, i, 616), and the conversion of *meso*-benzdianthrone into *meso*-naphthadianthrone (Scholl and Mansfeld, Abstr., 1910, i, 494). The method has been extended to the following cases.



(I.)

Phenyl α-naphthyl ketone is converted at 140° into benzanthrone. Similarly, 6 : 7-phthaloylbenzanthrone is obtained from 2-anthraquinonyl α-naphthyl ketone.

Dibenzoylpyrene is converted into pyranthrone, a synthesis which proves the benzoyl groups to occupy positions 3 and 8 in pyrene. Presumably oxidising agents act at these positions, so that pyrenequinone is 3 : 8-diketopyrene (formula I) and not 3 : 10-diketopyrene, as supposed by Bamberger and Philip (Abstr., 1887, 496) and by Goldschmiedt (Abstr., 1907, i, 310).



(II.)

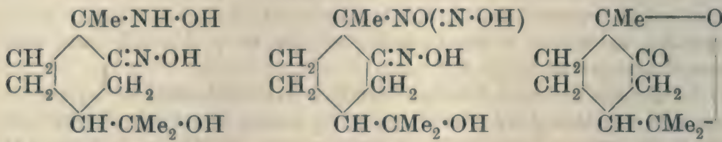
Dibenzpyranthrones are obtained on heating di-α- or di-β-naphthoylpyrenes. These dyes give in blue vats much redder shades than pyranthrone.

4 : 4′-Dibenzoyl-1 : 1′-dinaphthyl when heated at 95—100° with aluminium chloride yields violanthrone.

Heterocyclic rings are condensed in similar manner; thus from 3 : 8-di-α-thenoylpyrene, a thiophen analogue of pyranthrone (formula II) is obtained; this is a brownish-red product, which behaves like the vat dyes of the anthraquinone series. Benzil is converted into phenanthraquinone below 100°.

E. F. A.

Synthesis of a Ketone Derived from Cineole. GUIDO CUSMANO and ARRIGO LINARI (*Gazzetta*, 1912, **42**, i, 1—10).—The action of hydroxylamine on α-terpineol nitrosochloride yields the hydroxylamine-oxime (I). From this by means of nitrous acid, the *o-iso*nitroamine-oxime (II) is obtained. The *o-iso*nitroamineoxime when heated with water yields an oxime, $C_{10}H_{17}O_2N$, which when oxidised or treated with ethyl nitrite and subsequently with ammonia gives a ketone, $C_{10}H_{16}O_2$, of the constitution indicated in formula (III).

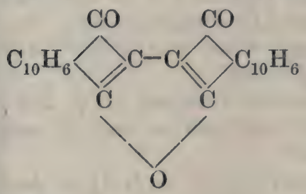


(I.) (II.) (III.)

α-*Terpineol*-o-*hydroxylamineoxime*, $C_{10}H_{20}O_3N_2$, is prepared in the same way as the other hydroxylamineoximes previously described (compare Cusmano, Abstr., 1910, i, 685, 863). It forms tufts of colourless, acicular crystals, m. p. 183° (decomp.). It condenses with *p*-nitrobenzaldehyde, yielding a yellow, crystalline *compound*, m. p. 183°. When treated with dilute hydrochloric acid and sodium nitrite in the cold, it yields the o-iso*nitroamineoxime*, $C_{10}H_{19}O_4N_3$, which forms colourless, prismatic crystals, which decompose at 156—157°. The substance yields a blood-red coloration with ferric chloride, and gives Liebermann's reaction. It dissolves in alkali carbonates, and forms crystalline *brucine* salts. When it is treated with an aqueous solution of an alkali hydroxide, nitrous oxide is evolved, and hydroxydihydrocarvoneoxime is formed quantitatively. When the *iso*nitroamine-oxime is heated with water alone, however, two other *oximes* are produced. One has the composition $C_{10}H_{19}O_3N,H_2O$, and m. p. 95°, the other has the composition $C_{10}H_{17}O_2N$, and m. p. 139—140°. In the presence of small quantities of mineral acids the *iso*nitroamine-oxime decomposes, yielding the oxime of m. p. 139—140°, hydroxydihydrocarvone, and the methyl ketone of homoterpenylic acid.

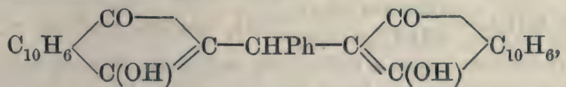
The oxime, $C_{10}H_{17}O_2N$, when treated with hydrobromic acid at the ordinary temperature yields the methyl ketone of homoterpenylic acid. Hydrochloric acid gives the *hydrochloride*, $C_{10}H_{17}O_2N,HCl$, and a product, which is decomposed by water with the formation of ammonium chloride and the methyl ketone of homoterpenylic acid. When the oxime, $C_{10}H_{17}O_2N$, is dissolved in ethyl nitrite, a *pernitrosyl* derivative, $C_{10}H_{16}O_3N_2$, is obtained; it forms large crystals, m. p. 68—70°. The *ketone*, $C_{10}H_{16}O_2$, is produced in small quantity by oxidising the oxime, $C_{10}H_{17}O_2N$, with acid permanganate, but is best prepared by decomposing the pernitrosyl derivative with concentrated ammonia. It crystallises in shining, colourless leaflets, and has a slight odour reminiscent of cineol. Its *semicarbazone*, $C_{10}H_{19}O_2N_3$, has m. p. about 220°. When oxidised with acid permanganate (1%), the ketone yields the methyl ketone of homoterpenylic acid almost quantitatively. Alkaline permanganate attacks it much less readily, the products being the above methyl ketone and cineolic acid. R. V. S.

Hydroxyketo*peri*naphthindene (*peri* - Naphthindandione). GIORGIO ERRERA and A. CUFFARO (*Gazzetta*, 1911, 41, ii, 807—814. Compare Errera, Abstr., 1911, i, 465).—Since the substance previously described under the name of *peri*-naphthindandione always behaves as a keto-enol containing the grouping –CO·CH:C(OH)–, and since no derivative of the corresponding diketonic form is known, and, moreover, the free substance contains an hydroxyl group, the authors propose to substitute for their original name that of hydroxyketo*peri*naphthindene. When the substance is oxidised with potassium dichromate and acetic acid (allowing one atom of oxygen per molecule), *anhydrobishydroxyketo*peri*naphthindene* (annexed formula) is obtained; it crystallises in yellowish-brown needles, which, on heating, blacken at 360° and melt with decomposition at a higher temperature. The oxidation of hydroxyketo*peri*naphthindene by means of alkaline permanganate proceeds quite differently. Even when less than the theoretical quantity of permanganate is taken, a vigorous reaction occurs, and the following substances are obtained: (1) unaltered hydroxyketo*peri*naphthindene; (2) naphthalic acid, and (3) a substance, $C_{13}H_8O_5$, which crystallises in tufts of very small, colourless needles, m. p. about 225° (decomp.). To this substance is assigned the constitution $CO_2H{\cdot}C_{10}H_6{\cdot}CO{\cdot}CO_2H$, and it is termed *naphthalonic acid.*

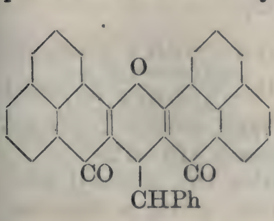


It is decomposed by heat in the same manner as is phthalonic acid (compare Graebe and Trümpy, Abstr., 1898, i, 318), naphthalic anhydride being formed, and also a substance, $C_{24}H_{14}O_5$, which is to be regarded as the *anhydride* of *naphthalaldehydic acid*; it has m. p. 310—313° (rapid heating), and is identical with a product obtained by Graebe and Gfeller (Abstr., 1893, i, 656).

When hydroxyketo*peri*naphthindene is boiled with benzaldehyde in alcoholic solution in presence of a trace of pyridine, *dihydroxyketo*peri*naphthindenilphenylmethane*,



is obtained; it is a golden-yellow, crystalline powder (from alcohol), or forms red crystals (from xylene), m. p. 295—297° (decomp.). The substance can give metallic derivatives, but both the sodium and potassium salts are very sparingly soluble in water. The *mono-sodium* salt, $C_{33}H_{19}O_4Na$, is a yellow, crystalline substance.



When dihydroxyketo*peri*naphthindenilphenylmethane is boiled with an alcoholic solution of sulphuric acid, a substance is precipitated to which the constitution of *phenyldiketo*peri*naphthindenexanthene* (annexed formula) is ascribed; it crystallises in yellow needles, melts with decomposition at

some temperature above 365°, and does not contain ethoxy-groups or form salts. R. V. S.

Transformation of a Phloroglucinol Derivative into One of *cyclo*Hexantrione. II. GUSTAV HELLER (*Ber.*, 1912, **45**, 418—427. Compare Abstr., 1909, i, 656).—The author gives a summary of reactions in which the ester of a phenol has been observed to suffer rearrangement into a hydroxy-ketone, and indicates that in the preparation of hydroxy-ketones by the condensation of acyl chlorides with phenols, the phenolic esters must be intermediate products.

In extension of the previous investigation (*loc. cit.*), it is observed that tribromophloroglucinyl triacetate, trichlorophloroglucinyl triacetate, and 1 : 3 : 5-triacetyltriaminobenzene when heated with zinc chloride show no sign of molecular rearrangement.

[With GEORG KRETZSCHMAR.]—*Phloroglucinol diacetate*, m. p. 104°, is obtainable by the action of phloroglucinol with sodium acetate and the theoretical quantity of acetic anhydride.

Triacetyl*cyclo*hexantrione is so resistant to complete hydrolysis that this does not occur without rearrangement. If it is dissolved in dilute sodium hydroxide solution, slow hydrolysis occurs; the precipitate obtained on acidifying is treated with boiling water, when the undissolved residue consists of *diacetyl*cyclo*hexantrione*; this crystallises from benzene in needles, m. p. 168°. This substance is also obtained as a by-product in the transformation of phloroglucinyl triacetate into the triacetyl*cyclo*hexantrione. *Tribenzoyldiacetyl*cyclo*hexantrione*, $CAcBz{<}{\begin{smallmatrix}CO-CHBz\\CO\cdot CAcBz\end{smallmatrix}}{>}CO$, obtained by benzoylation, crystallises in needles, m. p. 137—138°; it dissolves slowly in sodium hydroxide solution, but gives no coloration with ferric chloride. The action of a diazonium solution yields *benzeneazodiacetyl*cyclo*hexantrione*, $CHAc{<}{\begin{smallmatrix}CO——CHAc\\CO\cdot CH\cdot(N_2Ph)\end{smallmatrix}}{>}CO$, orange-coloured needle crystals, m. p. 209°. The action of nitrous acid gives *oximinodiacetyl*cyclo*hexantrione*, $CHAc{<}{\begin{smallmatrix}CO——CHAc\\CO\cdot C:(NOH)\end{smallmatrix}}{>}CO$, golden leaflets, m. p. 149°, which by reduction gives a colourless *substance*, decomposing at 200°.

The hot aqueous filtrate from the diacetyl*cyclo*hexantrione (above) on cooling deposits *monoacetyl*cyclo*hexantrione*; this gives pale rose-coloured crystals of a *monohydrate*, but when anhydrous it is colourless, m. p. 209—210°. Its *tribenzoyl* derivative,

$$CHBz{<}{\begin{smallmatrix}CO-CHBz\\CO\cdot CAcBz\end{smallmatrix}}{>}CO,$$

forms colourless needles, m. p. 116—117°; it reacts with a diazonium solution, forming a *bis-azo*-compound, $N_2Ph\cdot CH{<}{\begin{smallmatrix}CO——CHAc\\CO\cdot CH(N_2Ph)\end{smallmatrix}}{>}CO$, purple needles, m. p. 241—242° (decomp.). With nitrous acid a *bis-oximino*-compound is obtained, which decomposes at 115—120°.

Di- and mono-acetyl*cyclo*hexantrione resemble the triacetyl compound in dissolving in sodium hydroxide solution, giving a coloration

with ferric chloride, and in forming copper salts; the acid character is more marked the fewer the acetyl groups present. All three substances react with benzaldehyde in alkaline alcoholic solution, producing yellow, amorphous substances. Towards phenylhydrazine and hydroxylamine they are inert, whilst bromine attacks them all, the monoacetyl compound most readily. D. F. T.

Certain Derivatives of Tetrachloro-*o*-benzoquinone. C. LORING JACKSON and GEORGE LESLIE KELLEY (*Amer. Chem. J.*, 1912, **47**, 197—221).—A continuation has been made of the study of three substances prepared from tetrachloro-*o*-benzoquinone (Jackson and MacLaurin, Abstr., 1907, i, 856).

The compound, m. p. 215°, obtained by the action of benzyl alcohol on tetrachloro-*o*-benzoquinone, has proved to be the heptachloro-*o*-quinocatechol hemiether described by Jackson and Carleton (Abstr., 1908, i, 428). This was confirmed by analyses of its acetyl derivative, m. p. 195°, its reduction product (heptachlorodihydroxycatechol hemiether), m. p. about 188—190°, and the *triacetyl* derivative,

$$OAc\cdot C_6Cl_4\cdot O\cdot C_6Cl_3(OAc)_2,$$

m. p. 144°, which forms white, hexagonal prisms.

The other two compounds investigated were those, m. p. 198° and 210°, which were respectively obtained by the action of methyl and ethyl alcohol on tetrachloro-*o*-benzoquinone. They can also be prepared by the action of the alcohols on heptachloro- or hexachloro-*o*-quinocatechol hemiether.

The methyl compound was originally regarded as hexachloro-*o*-benzoquinomethylhemiacetalcatechol ether, $C_6Cl_4O_2{:}C_6Cl_2O(OH)(OMe)$, on account of its being produced by the action of methyl alcohol on the ether, $C_6Cl_4O_2{:}C_6Cl_2O_2$, but has now been found to be *hexachloromethoxy-o-quinocatechol hemiether*, $OH\cdot C_6Cl_4\cdot O\cdot C_6Cl_2O_2(OMe)$. On reducing the compound with zinc dust and sulphurous acid, it was converted into *hexachloromethoxy-o-dihydroxycatechol hemiether*,

$$OH\cdot C_6Cl_4\cdot O\cdot C_6Cl_2(OH)_2(OMe),$$

m. p. 191°, which crystallises in long, colourless needles, and yields a *triacetyl* derivative, m. p. 128—129°, and a *monoacetyl* derivative, m. p. 186—188°. In the course of preparing these acetyl compounds another compound was obtained, m. p. 122°.

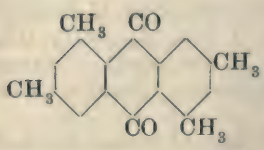
The compound, m. p. 210°, obtained by the action of ethyl alcohol on tetrachloro-*o*-benzoquinone, has been found to be *hexachloroethoxy-o-quinocatechol hemiether*, $OH\cdot C_6Cl_4\cdot O\cdot C_6Cl_2O_2(OEt)$; its *acetyl* derivative has m. p. 195°. On reducing the compound with sulphurous acid, it is converted into *hexachloroethoxy-o-dihydroxycatechol hemiether*,

$$OH\cdot C_6Cl_4\cdot O\cdot C_6Cl_2(OH)_2(OEt),$$

m. p. 173°, which forms white needles, and yields a *triacetyl* derivative, m. p. 165°. If, however, the reduction is effected by zinc and acetic acid, a *compound*, m. p. 249°, is produced, and readily undergoes decomposition with formation of hexachloro-*o*-dihydroxycatechol ether, which furnishes an *acetyl* derivative, $C_6Cl_4O_2{:}C_6Cl_2(OAc)(OH)$, m. p. 251°, as well as the diacetyl derivative described previously.

E. G.

Method of Formation of Alkylated Anthraquinones from Alkylated Benzoyl Chlorides and Aluminium Chloride. II. CHRISTIAN SEER [with EGON EHRENZWEIG] (*Monatsh.*, 1912, 33, 33—34. Compare Abstr., 1911, i, 386).—Mesitylenyl chloride, $C_6H_3Me_2\cdot COCl$, reacts when heated with aluminium chloride at 115—120° to give 1 : 3 : 5 : 7-tetramethylanthraquinone. The compound so obtained differs from all other anthraquinone derivatives in that it is not reduced by alkaline sodium hyposulphite or by zinc dust and sodium hydroxide. It is not attacked by acetyl or benzoyl chloride or by phosphorus pentachloride, and when distilled with zinc dust, tetramethylanthracene is obtained.



The structure is confirmed by the synthesis from *m*-xylyl mesityl ketone, which was heated for some days, the tetramethylanthracene formed separated by distillation, and oxidised with acetic and chromic acids to the quinone.

1 : 3 . 5 : 7-Tetramethylanthraquinone is not identical with the substance obtained by Dewar and Jones (Trans., 1904, 85, 212) by the action of nickel carbonyl on *m*-xylene, to which they ascribe the same constitution. It is, however, the same as the oxidation product of the tetramethylanthracene obtained by Friedel and Crafts (Abstr., 1887, 1102) from the reaction of methylene chloride and *m*-xylene in presence of aluminium chloride. It is now found that a little of the isomeride described by Dewar and Jones is produced at the same time; the constitution of 1 : 3 : 6 : 8-tetramethylanthraquinone is ascribed to this.

1 : 3 : 5 : 7-Tetramethylanthraquinone forms yellow needles, m. p. 235°; it dissolves in concentrated sulphuric acid with a dark red coloration. The corresponding 1 : 3 : 5 : 7-tetramethylanthracene forms yellowish-white platelets, m. p. 155—157°, or when purified by regeneration from the picrate, m. p. 163—164°. The *picrate* has m. p. 189—190°.

Anthraquinone-1 : 3 : 5 : 7-tetracarboxylic acid and its salts were obtained amorphous, m. p. above 300°.

4 : 8-*Dinitro*-1 : 3 : 5 : 7-*tetramethylanthraquinone*, prepared by the action of potassium nitrate and concentrated sulphuric acid on the quinone, separates in greyish-brown needles, m. p. 296°. 2 : 4 : 6 : 8-*Tetranitro*-1 : 3 : 5 : 7-*tetramethylanthraquinone* crystallises in yellow, microscopic plates. E. F. A.

Action of Ammonia on Chrysophanic Acid Methyl Ether. OTTO A. OESTERLE (*J. pr. Chem.*, 1912, [ii], 85, 230—232. Compare Abstr., 1910, i, 860).—It is pointed out that Fischer and Gross (Abstr., 1911, i, 886) have erroneously attributed to the author the view that the action of ammonia on chrysophanic acid monomethyl ether leads to the replacement of the hydroxyl by an amino-group. The product of the action crystallises in long, glistening, brownish-red needles, m. p. 237—239°, and has the constitution of a 1-hydroxy-8-methoxymethylanthraquinoneimide. F. B.

Commercial Chrysarobin. OSWALD HESSE (*Annalen*, 1912, **388**, 65—96. Compare Tutin and Clewer, Trans., 1912, **101**, 290).—Commercial chrysarobin is demethylated by hydriodic acid, D 1·7, at 120—125°, or by equal volumes of hydrochloric acid, D 1·19, and glacial acetic acid at 130—140°, and the dried product is boiled with petroleum (which extracts a portion of the chrysophanol) and then with chloroform, in which chrysophanol in much more soluble than emodinol.

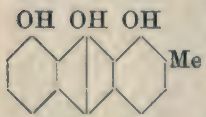
Chrysophanol, $C_{15}H_{12}O_3$ (previously called chrysarobin by the author and by Jowett and Potter, Trans., 1902, **81**, 1575), has m. p. 204° (not 205—210°, as stated previously). The presence of a small amount of the methyl ether lowers the m. p. by 6—8°, and of emodinol raises it by about the same amount (compare Fischer, Falco, and Gross, Abstr., 1911, i, 886). It is insoluble in alkali hydroxides or carbonates in the absence of air. By the admission of air, chrysophanol dissolves with the formation of chrysophanic acid; the latter is also formed by oxidising the anthranol with chromic and acetic acids at 60—70°. When heated with acetic anhydride at 90—100° for four hours, with occasional boiling for periods of ten minutes, chrysophanol yields a *triacetate*, m. p. 238—240° (Jowett and Potter's diacetate, *loc. cit.*), which is converted into diacetylchrysophanic acid, m. p. 208° (Liebermann and Seidler's "acetylchrysarobin") by acetic and chromic acids at 60—70°. Triacetylchrysophanol, like diacetylchrysophanic acid, yields diacetylrhein by oxidation with chromic acid in a hot solution of equal volumes of acetic acid and acetic anhydride (compare Fischer, Falco, and Gross, *loc. cit.*). *Hexa-acetyldichrysophanol*, m. p. 125°, is a by-product of the acetylation of chrysophanol.

Emodinol, $C_{15}H_{12}O_4$, isolated as described above, has m. p. 230—240° (decomp.), and yields *acetylemodinol*, $C_{15}H_{11}O_4Ac$, m. p. 199°, yellow leaflets, by heating with acetic anhydride at 90—100° for two hours. Emodinol and acetylemodinol yield emodin and acetylemodin respectively by oxidation with chromic and acetic acids. The acetylation of emodinol by acetic anhydride and sodium acetate at 90—100° for two hours yields *tetra-acetylemodinol*, $C_{15}H_8O_4Ac_4$, m. p. 197°, yellow prisms, *octa-acetyldiemodinol*, $C_{30}H_{16}O_8Ac_8$, m. p. 125°, yellow powder, being formed as a by-product, The tetra-acetate is oxidised by chromic (calculated quantity) and acetic acids at 50—60° to triacetylemodin, which is converted into triacetylemodic acid by chromic acid, acetic acid, and acetic anhydride at 60—70°. Octa-acetyldiemodinol is converted into triacetylemodin by chromic and acetic acids at 60—70°.

Chrysarobol, $C_{15}H_{12}O_4$, m. p. 250—252°, almost colourless needles, is obtained from the portion of commercial chrysarobin which is insoluble in ethyl acetate at 55°. It is unattacked by boiling, concentrated nitric acid, does not yield methyl iodide with hydriodic acid, dissolves in aqueous potassium hydroxide with a yellow colour, and in concentrated sulphuric acid with a purple-red colour changing to reddish-brown. It is insoluble in alcohol, and therefore does not develop a coloration with alcoholic ferric chloride. It yields β-methylanthracene by reduction with zinc dust. It is converted into *acetylchrysarobol*, $C_{15}H_{11}O_4Ac$, m. p. about 245°, yellow needles, by hot acetic anhydride, and into *tetra-acetylchrysarobol*, $C_{15}H_8O_4Ac_4$, m. p. about 190°, greenish-yellow flocks, by acetic anhydride and

sodium acetate at 90—100°. The tetra-acetate is oxidised by chromic and acetic acids at 50° to a red, amorphous *substance*, which does not yield emodin by hydrolysis. The substance, which crystallises from the ethyl acetate extracts of commercial chrysarobin (obtained in the isolation of chrysarobol), consists essentially of emodinol methyl ether.

It is seen from the preceding that commercial chrysarobin contains chrysophanol and its methyl ether, emodinol and its methyl ether, and chrysarobol. Of these, only the first and the last can be isolated directly and pure. These results are confirmed by the direct oxidation of chrysarobin, with and without previous acetylation or demethylation. By direct oxidation, by oxygen in alkaline solution, or by chromic and acetic acids, chrysarobin yields chrysophanic acid and emodin and their methyl ethers. When acetylated and subsequently oxidised by chromic acid, chrysarobin yields diacetylchrysophanic acid, diacetylemodin methyl ether, acetylchrysophanic acid methyl ether, and a small quantity of a *substance*, m. p. 202°, orange-yellow needles, which is probably *chrysarobic acid*.



The paper closes with a discussion of the constitutions of some of the preceding anthranols. Chrysophanol has probably the annexed formula, not that previously given (compare Oesterle, Abstr., 1911, i, 887). C. S.

Derivatives of Menthone. EYVIND BÖDTKER (*Compt. rend* 1912, 154, 437—439. Compare Abstr., 1907, i, 857).—The constitution previously ascribed to the compounds obtained by acting on benzylidenementhone with magnesium alkyl bromides is confirmed by an examination of their oxidation products.

When benzylidenementhone is treated with magnesium methyl iodide and benzoyl chloride added before the addition of water, *phenylmenthylmethylmethane benzoate*, $C_8H_{16}<\begin{matrix}C\cdot CHMePh \\ \| \\ C\cdot OBz\end{matrix}$, is formed, having m. p. 152—153°, $[\alpha]_D^{20\cdot5}$ 145°40′; on hydrolysis it yields *phenylmenthylmethylmethane*, $C_8H_{16}<\begin{matrix}CH\cdot CHPhMe \\ | \\ CO\end{matrix}$, m. p. 111—112°, $[\alpha]_D^{19}$ +95°16′. *Phenylmenthyl*isoamyl*methane*, $C_{21}H_{32}O$, is a viscous liquid, b. p. 215°/15 mm., $[\alpha]_D^{20\cdot5}$ +13°45′, $n_D^{22\cdot2}$ 1·50568; the *benzoate* has m. p. 93—94°, $[\alpha]_D^{19\cdot5}$ +186°29′. *Benzoylmenthone*, $C_{17}H_{22}O_2$, was obtained as a yellow liquid by treating a toluene solution of menthone successively with sodamide and benzoyl chloride; it has b. p. 185°/12 mm., $[\alpha]_D^{20\cdot5}$ +32°11′, n_D 1·51745.

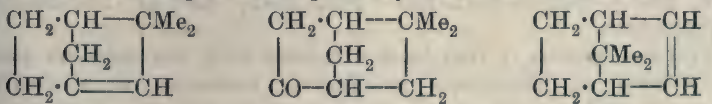
The rotations given are for benzene solutions. W. O. W.

The Camphenilone Group. II. *iso*Camphenilone and Constitution of Camphenilene and of *apo*Bornylene. S. V. HINTIKKA and GUSTAV KOMPPA (*Annalen*, 1912, 387, 293—316. Compare Abstr., 1909, i, 500).—The generally accepted view that camphenilone and fenchone are homologous is further strengthened by the conversion of the former into *iso*camphenilone through the following

series of compounds, the change being quite analogous to that whereby fenchone has been converted into *iso*fenchone.

Camphenilone, the preparation of which from camphene by a very simple process is described, is reduced to camphenilol, a camphenilone pinacone, m. p. 146°, being obtained as a by-product. Camphenilol, which forms a *benzoate*, $C_9H_{15}\cdot OBz$, b. p. 172°/15 mm., is converted into camphenilene by phosphoric oxide at 140—150°. Camphenilene has also been prepared by converting camphenilol into camphenilyl chloride and heating this with aniline at 175—180°, with diethylaniline at 180—185°, with alcoholic potassium hydroxide, or, most frequently, by direct distillation with aniline after the mixture has been boiled under reflux for five hours. The hydrocarbon obtained by these processes has b. p. 140—141°, D_4^{20} 0·8693, n_D^{20} 1·46848, n_γ^{20} 1·47850, n_β^{20} 1·47425, and n_α^{20} 1·46507. Camphenilene forms a *hydrochloride*, $C_9H_{15}Cl$, m. p. 60—61°, needles or plates (which is probably identical with camphenilyl chloride, since mixtures of the two substances show no depression of the m. p.), and a *nitrosite*, $C_9H_{14}O_3N_2$, m. p. 122° (decomp.), bluish-green prisms, and is converted by the Bertram-Walbaum mixture of acetic and sulphuric acids at 50—55° into an *acetate*, $C_9H_{15}\cdot OAc$, b. p. 195°, the hydrolysis of which by alcoholic potassium hydroxide yields iso*camphenilol*, $C_9H_{15}\cdot OH$, b. p. 196°, m. p. 78°. This alcohol forms a *benzoate*, m. p. 79°, *phenylcarbamate*, m. p. 65°, and *hydrogen phthalate*, m. p. 118—119°, and is oxidised by potassium dichromate and dilute sulphuric acid to iso*camphenilone*, $C_9H_{14}O$, m. p. 55—57°, large, white plates (*semicarbazone*, m. p. 225—226°, clusters of short, monoclinic prisms).

Camphenilene in glacial acetic acid yields with 17% ozone an *ozonide*, by the distillation of which in a vacuum is obtained a *keto-aldehyde*, $C_9H_{14}O_2$, b. p. 123—125°/15 mm., D_4^{22} 1·0325, n_α^{22} 1·46571, n_D^{22} 1·46867, n_γ^{22} 1·47969, which reduces Fehling's and ammoniacal silver solutions, forms a *disemicarbazone*, m. p. 205—206°, and by further oxidation with ozone yields a *keto-acid*, $C_7H_{13}(CO)\cdot CO_2H$. These results prove that camphenilene must have the constitution (I), assuming that Wagner's camphenilone formula is correct. Moreover, it follows that *iso*camphenilone probably has the constitution (II).



(I.) (II.) (III.)

Finally, since *apo*bornylene, which is also derived from camphenilone, yields by ozonisation an ozonide by the decomposition of which is obtained a di-aldehyde which oxidises to *apo*camphoric acid in the air, it follows that *apo*bornylene has the constitution (III); the formation of a substance of this constitution from camphenilone (Wagner's formula) is readily explicable. C. S.

Rotatory Power of Camphor in Carbon Tetrachloride Solution. A. FAUCON (*Compt. rend.*, 1912, 154, 652—655).—The specific rotatory power of camphor in solutions of carbon tetrachloride of different concentrations is given, together with empirical formulæ

expressing the connexion between rotation and concentration. For solutions containing 25—55 grams per 100 c.c. of solvent, $[\alpha]_D^{15} = 43{\cdot}56° + 0{\cdot}1148°c$. The variation in rotatory power with temperature depends on concentration, especially when this is high. The increase for a rise of 1° is greater at 12° than at 40°. W. O. W.

The Principal Constituents of Labdanum Oil. Ketonic Compounds. HENRI MASSON (*Compt. rend.*, 1912, **154**, 517—519).—Gum labdanum from *Cistus creticus* or *C. ladaniferus* gave 0·7—0·9% of a yellow oil when distilled in steam. The oil had b. p. 50—185°/15 mm., and contained alcohols, phenols, esters, terpenes, and ketones. The latter were removed, and on fractionation yielded acetophenone and a fraction, b. p. 70—78°/15 mm., containing 1 : 1 : 5-*trimethyl*cyclo*hexanone*, $C_9H_{16}O$. When regenerated from the *oxime* (m. p. 106°, b. p. 126—127°/17 mm.) this was obtained as a liquid, b. p. 66—67°/10 mm., 178—179°/760 mm., D 0·922, n_D^{23} 1·4494. It does not form a bisulphite compound, but yields a *semicarbazone*, m. p. 220—221°, and a *monobromo*-derivative, m. p. 41°. Reduction with sodium and alcohol gives 1 : 1 : 5-*trimethyl*cyclo*hexanol*, m. p. 51°, b. p. 87°/28 mm. Oxidation with potassium permanganate leads to the formation of *ε-keto-αα-dimethylhexoic acid*,

$$COMe{\cdot}[CH_2]_3{\cdot}CMe_2{\cdot}CO_2H,$$

b. p. 190—191°/31 mm. (*semicarbazone*, m. p. 164°). The constitution of the acid was established by converting it into αα-dimethyladipic acid by means of sodium hypobromite. W. O. W.

Bee Resin (Propolis). KARL DEITERICH (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 315—318. Compare Küstenmacher, Abstr., 1911, ii, 127).—Extraction of propolis with light petroleum removes wax and balsam, and these are separated by means of 70% alcohol. Resin, m. p. 90—106°, is extracted from the residue by absolute alcohol, and tannin is then extracted from the resin by water. The resin is then extracted with cold absolute alcohol, when an insoluble residue, proporesen, remains. Ether precipitates α-proporesen from the solution, and the filtrate after evaporation is separated by chloroform into a soluble part, the "pure resin," and an insoluble part, β-proporesen.

Propolis balsam is free from cinnamic acid, but contains vanillin. Proporesen is chemically indifferent, fluoresces in concentrated sulphuric acid, sinters at 76° and has m. p. 83°, and is insoluble in chloral hydrate solution. α-Proporesin has m. p. 187°, and is not fluorescent in sulphuric acid. β-Proporesin is completely soluble in chloral hydrate solution, fluoresces in sulphuric acid, and yields an alcohol on hydrolysis. The acid sublimes in needles, sinters at 88—90°, and melts at 124—125°. The "pure resin" fraction is also fluorescent, and yields an acid and a resinotannol on hydrolysis.

C. H. D.

Structure of Polymerised Vinyl Bromide and Caoutchouc. IWAN I. OSTROMISSLENSKY (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 204—240).—The author shows that polymerised vinyl bromide (compare Hofmann, *Annalen*, 1860, **115**, 271; Baumann, *Annalen*, 1872,

163, 315), to which he gives the name *caouprene bromide*, exists in three modifications possessing identical chemical but different physical properties, and readily convertible one into the others. Caouprene bromide is a simpler homologue of the bromide of natural Para caoutchouc, which contains methyl groups; further, it is either identical with butadiene-caoutchouc bromide (compare Harries, Abstr., 1911, i, 798) or isomeric with it, the isomerism being due to a difference in the distribution of the halogen atoms in the molecule. The compounds obtained by the action of aniline or phenols on these bromides and the hydrocarbon resulting from the removal of hydrogen bromide from them are also discussed.

α-Caouprene bromide is alone formed by the action of sunlight on vinyl bromide, the velocity of the polymerisation being dependent in high degree on the presence of traces of contact substances, which may either retard or accelerate the change; hydrocarbons of low boiling point, such as light petroleum, retard or even arrest completely the reaction. The α-bromide dissolves readily in carbon disulphide and a number of other solvents, from some of which it may be precipitated in the form of asbestos-like threads, from others in an amorphous state, and from others as a milky emulsion. It resists the action of energetic oxidising agents, concentrated alcoholic potassium hydroxide, and concentrated mineral acids.

β- and γ-Caouprene bromides are obtained by the action of the ultraviolet light of a quartz-mercury lamp on vinyl bromide, best in the gaseous state. The β-compound is soluble in carbon disulphide, but the γ-bromide is quite insoluble, and merely swells up in this solvent and forms two layers, the upper one of pure carbon disulphide and the lower, which shows intense violet fluorescence, of the gelatinous bromide retaining a considerable proportion of the solvent.

On prolonged heating at 50° of the α-bromide or boiling of its carbon disulphide solution, isomeric change into the β-form takes place. The change α- $\longrightarrow$ β- $\longrightarrow$ γ-modification is readily brought about by ultraviolet light or by protracted boiling with anhydrous acetic acid. The γ- may be changed completely into the β-bromide by dissolving in boiling chlorobenzene and precipitating with light petroleum.

The compound described by Harries (*loc. cit.*) as butadiene-caoutchouc tetrabromide is also found to exist in three modifications, one of which does not dissolve, but swells, in carbon disulphide, forming a fluorescent jelly. The other two forms are soluble in carbon disulphide, in which one gives a fluorescent and the other a non-fluorescent solution.

The tetrabromide of neutral Para caoutchouc, which is homologous with caouprene bromide, also exists in certain analogous modifications (compare Weber, Abstr., 1900, i, 353). Free Para caoutchouc is likewise obtainable in three forms (Harries, *loc. cit.*), which are probably due to the same cause as the three caouprene bromides and the three butadiene-caoutchouc bromides, since in all three cases the interconversions take place under similar conditious. The differences between the three modifications of any one of these compounds are probably due to differences in the physical structures of their mole-

cules, for example, such differences as exist between sodium chloride in the ordinary and colloidal states. In some instances, however, the variation in properties seems to depend on the absence or presence, in the surface layers, of oxidation products.

β- and γ-Caouprene bromides give exclusively colloidal solutions, as is shown by the boiling and freezing points of their solutions. Cryoscopic measurements in ethylene dibromide indicate for α-caouprene bromide the molecular weight 1809, corresponding with

$$(\cdot CH_2\cdot CHBr\cdot)_{16}.$$

Each of the three caouprene bromides, and also butadiene-caoutchouc bromide, react with phenol at 150° (compare Weber, *loc. cit.*), giving a reddish-violet, elastic, amorphous compound, $(CH_2\cdot CH\cdot OPh)_n$.

When an aniline solution of caouprene bromide is heated, it assumes a cherry-red colour, the quaternary ammonium salt,

$$(CH_2\cdot CH)_n(NH_2Ph)_{n/2}Br_{n/2},$$

being formed. Rapid cooling of the solution results in the deposition of a spongy mass, to which the name meta-*caouprene bromide* is given: $(CH_2\cdot CH)_n(NH_2Ph)_{n/2}Br_{n/2} =$ meta-$(CH_2\cdot CH)_nBr_{n/2} + n/2NH_2Ph$. The meta-bromide dissolves readily in carbon disulphide at the ordinary temperature giving an intensely fluorescent, violet solution, and, unlike the normal bromide, dissolves readily in fused phenol with formation of a pale brown solution, from which benzene precipitates a brown powder; normal caouprene bromide gives an intense violet solution with phenol, the compound $(CH_2\cdot CH)_n(OPh)_{n/2}$ being formed. The rearrangement of halogen atoms, to which the formation of the meta-bromide is due, is not effected by quinoline, caouprene bromide precipitated from this solvent retaining its original chemical and physical characters.

When a 10% solution of caouprene bromide in aniline is heated for thirty minutes at 120—130° out of contact with air, subsequent precipitation with alcohol or ether yields a new bromo-compound which does not give Weber's reaction with phenol. This compound, which has not yet been obtained pure and is apparently non-homogeneous, dissolves in fused phenol to a pale, reddish-yellow solution not precipitated by benzene; when heated in nitrobenzene it gives up hydrogen bromide.

The removal of hydrogen bromide from caouprene bromide, its *meta*-modification, butadiene-caoutchouc bromide, and the bromide of natural caoutchouc leads to the formation of a hydrocarbon, $(CH)_n$, and may be effected in various ways: (1) by prolonged heating with water in sealed tubes at 150°; (2) by heating solutions of the bromides in various solvents, such as aniline, quinoline, dichloroacetic acid, aromatic nitro-derivatives, etc., best in absence of air; the influence of these organic compounds on the removal of hydrogen bromide from the molecule of the complex bromide depends, not entirely on their power of dissolving the latter or the hydrocarbon formed, but also on their ability to absorb the hydrogen bromide.

From a consideration of the above results, of the possible compounds obtainable by the polymerisation of vinyl bromide and of the fact that Weber's colour reaction with phenol is given by bromides of the terpene series in which the number of halogen atoms is a multiple of four, the

conclusion is drawn that the formation of caouprene bromide takes place according to the scheme :

$$n(\mathrm{CH_2{:}CHBr}) = (\cdot\mathrm{CH_2\cdot CHBr}\cdot)_n \longrightarrow$$

$$\begin{array}{l} \mathrm{CH_2\cdot CHBr\cdot CH_2\cdot CHBr\cdot CH_2\cdot CHBr\cdot CH_2\cdot CHBr} \\ \mathrm{CHBr\cdot CH_2}\cdot\cdots\cdots\cdots\cdots\cdots\cdot\mathrm{CHBr\cdot CH_2} \end{array}$$

(the dotted line representing an unknown number of $\cdot CH_2\cdot CHBr\cdot$ groups), the value of n being not less than 12. The alternate distribution of the bromine atoms is rendered probable by the fact that the autopolymerisation of halogen derivatives of ethylene or acetylene yields exclusively symmetrical trihalogen compounds of benzene; bromoacetylene, for example, gives 1 : 3 : 5-tribromobenzene.

The hydrocarbon, *dehydrocaouprene*, obtained by the removal of hydrogen bromide from caouprene bromide and its isomerides, is regarded as a higher homologue of benzene of the formula :

$$\begin{array}{l} \mathrm{CH{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CH} \\ \mathrm{CH{:}}\cdots\cdots\cdots\cdots\cdots\cdots\cdots\mathrm{{:}CH} \end{array}$$

The action of aniline on caouprene bromide and the subsequent decomposition of the quaternary ammonium compound thus obtained into aniline and *meta*-caouprene bromide are represented as follows :

$$\begin{array}{l} \mathrm{CH_2\cdot CHBr\cdot CH_2\cdot CHBr} \\ \mathrm{CHBr}\cdots\cdots\cdots\mathrm{CH_2} \end{array} + \mathrm{NH_2Ph} \longrightarrow$$

$$\begin{array}{l} \mathrm{CH_2\cdot CH(NH_2PhBr)\cdot CH_2\cdot CH\cdot NH_2PhBr} \\ \mathrm{CH(NH_2PhBr)}\cdots\cdots\cdots\mathrm{CH_2} \end{array} \longrightarrow$$

$$\mathrm{NH_2Ph} + \begin{array}{l} \mathrm{CH_2\cdot CHBr\cdot CHBr\cdot CH_2} \\ \mathrm{CHBr}\cdots\cdots\cdots\cdots\mathrm{CH_2} \end{array}.$$

In view of the results of Hinrichsen and Kindscher (Abstr., 1911, ii, 445) and of Pickles (Trans., 1910, 97, 1085), the statement made by Harries that caoutchouc must be regarded as an associated dimethyl*cyclo*octadiene of the form :

$$\begin{array}{l} \mathrm{CMe\cdot CH_2\cdot CH\cdot CH{-}CMe\cdot CH_2\cdot CH_2\cdot CH}\cdots\cdots\mathrm{CMe\cdot CH_2\cdot CH_2\cdot CH} \\ \mathrm{CH\cdot CH_2\cdot CH_2{-}CMe\cdot CH{-}CH_2{-}CH_2{-}CMe}\cdots\cdots\mathrm{CH\cdot CH_2{-}CH_2{-}CMe} \end{array}$$

is admissible only on the assumption that, when caoutchouc is brominated, it undergoes preliminary splitting with formation of dimethyl*cyclo*octadiene. The author hence regards this formula as discordant with the facts.

The most probable structure for caoutchouc bromide is :

$$\begin{array}{l} \mathrm{CH_2\cdot CHBr\cdot CMeBr\cdot CH_2\cdot CH_2\cdot CHBr\cdot CMeBr\cdot CH_2} \\ \mathrm{CH_2\cdot CHBr\cdot CMeBr}\cdot\cdots\cdots\cdots\mathrm{CH_2\cdot CMeBr\cdot CH_2} \end{array},$$

which is similar to the formula given by Pickles.

The polymerisation of isoprene to caoutchouc is best represented thus :

$$n(\mathrm{CH_2{:}CMe\cdot CH{:}CH_2}) = (\cdot\mathrm{CH_2\cdot CMe{:}CH\cdot CH_2}\cdot)_n =$$

$$\begin{array}{l} \mathrm{CH_2\cdot CMe{:}CH\cdot CH_2\cdot CH_2\cdot CH{:}CMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH} \\ \mathrm{CH_2\cdot CH{:}CMe\cdot CH_2\cdot CH_2\cdot CH{:}CMe}\cdot\cdots\cdots\cdot\mathrm{CH_2\cdot CMe} \end{array}.$$

The positions of the double linkings are here fixed, and isomerism is possible only in so far as the positions of the methyl groups are concerned.

The name caoutchouc tetrabromide is irrational, this compound

being at the least a hexabromide of the formula $C_{15}H_{24}Br_6$; for the present it is best termed simply caoutchouc bromide.

The various properties of caouprene bromide, synthetic butadiene-caoutchouc bromide, and natural Para caoutchouc bromide are collected in tabular form.

Willstätter and Waser's results (this vol., i, 17), published after the author's paper was in the press, compel the assumption that dehydrocaouprene is not a higher homologue of benzene, but that it has the following structure, or one similar to it:

$$\begin{array}{l} CH\cdot CH\cdot CH\cdot CH\cdot CH\cdots\cdots\cdots CH \\ CH\cdot CH\cdot CH\cdot CH\cdot CH\cdots\cdots\cdots CH \end{array}.$$

T. H. P.

Regeneration of Caoutchouc from its Bromide. Synthesis of Butadiene-caoutchouc. IWAN I. OSTROMISSLENSKY (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 240—244. Compare preceding abstract).—The action of zinc dust on caouprene bromide or butadiene-caoutchouc bromide dissolved in either naphthalene or chlorobenzene yields free caoutchouc, possessing identical chemical and physical properties in the two cases. The action of sodium on these bromides, especially in presence of ether, proceeds to some extent in the same direction, but is complicated by secondary processes, such as the formation of dehydrocaouprene, $(CH)n$. The action of sodium on a 2·3% solution of caouprene bromide in chlorobenzene containing a little ether is accompanied by sudden heating, the solvent boiling vigorously, and the chlorobenzene (which alone is quite inactive towards sodium) as well as the caouprene bromide being acted on by the sodium.

The solution of caouprene bromide or butadiene caoutchouc bromide in naphthalene or chlorobenzene shows a violet-red fluorescence.

As caouprene bromide is readily obtainable from alcohol, the above reaction leads to a new synthesis of butadiene caoutchouc:

$$CH_3\cdot CH_2\cdot OH + Al_2O_3 \longrightarrow CH_2{:}CH_2 \longrightarrow CH_2Br\cdot CH_2Br + KOH \longrightarrow$$

$$CH_2{:}CHBr \longrightarrow \begin{array}{l} CH_2\cdot CHBr\cdot CH_2\cdot CHBr \\ CHBr\cdots\cdots\cdots\cdots\cdot CH_2 \end{array} + Zn \longrightarrow \text{butadiene-caoutchouc.}$$

T. H. P.

Sphingosine. PHŒBUS A. LEVENE and WALTER G. JACOBS (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxix; *J. Biol. Chem.*, 11).—Sphingosine, obtained originally from phrenosin by Thudichum, appears to be an unsaturated amino-alcohol of the olefine series. The substance obtained later by Thierfelder in the filtrate from sphingosine sulphate and described by him as a nameless base is dimethylsphingosine. Full data will be published later. W. D. H.

Physcion. OSWALD HESSE (*Annalen*, 1912, 388, 97—102).—Physcion (parietin) yields emodin by demethylation by concentrated sulphuric acid at 160°. It is demethylated and also reduced by hydriodic acid, D 1·7, yielding a substance (protophyscihydron), m. p. 230—240°, which is shown to be emodinol by its conversion by acetylation into tetra-acetylemodinol, m. p. 198°, which yields

triacetylemodin by oxidation by chromic and acetic acids. The further proof that physcion is emodin methyl ether (compare Oesterle and Johann, Abstr., 1910, i, 860) is given by its methylation, whereby emodin trimethyl ether, m. p. 226°, is obtained. Physcihydron, the product of the reduction of physcion by zinc and acetic acid, is proved to be emodinol methyl ether by its conversion into triacetylemodinol methyl ether. C. S.

Duality of Chlorophyll. C. A. JACOBSON and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1912, *A*, 28—40; *Amer. Chem. J.*, 1912, **47**, 221—231).—Evidence is given to support the contention that the ratio of chlorophyll to *allo*chlorophyll varies with different species of plants, and also with changing conditions of growth of the same species. The actual amount of *allo*chlorophyllan, the nearest acid derivative of *allo*chlorophyll, isolated from a given weight of chlorophyllan from *Acer platanoides* of different years is very different. The absorption bands in the visible spectrum of the chlorophyllans obtained by identical methods from different species differ considerably. The same applies to the chlorophyllan bands in the ultra-violet part of the spectrum. The extinction coefficients, in monochromatic light, of equally concentrated solutions of chlorophyllans from different species vary considerably. The variable ratio between the two constituents of chlorophyll ranges from almost pure *allo*chlorophyll in *Acer negundo* to a product very rich in *neo*chlorophyll in the nettle.
E. F. A.

Chlorophyll. XIX. Chlorophyllides. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1912, **387**, 317—386).—The isolation of pure chlorophyll is difficult on account of its solubility, decomposibility, and chemical indifference. So far as the degradation of chlorophyll is concerned, the phytyl group is without significance. Hence for working out the early steps of the degradation of chlorophyll, it is convenient to use the substance in the form of the sparingly soluble, crystalline alkylchlorophyllides. Hitherto, no description and analyses of an individual chlorophyll derivative have been given, the crystallised ethylchlorophyllide previously described (Abstr., 1911, i, 659) being a mixture of the *a* and *b* compounds. The authors have now succeeded in separating methylchlorophyllides *a* and *b* from one another, and also in the separation of the chlorophyllides *a* and *b*, the methylphæophorbides *a* and *b*, and the phæophorbides *a* and *b*. The mixture of methylchlorophyllides *a* and *b* has been obtained by the methanolysis of the fresh leaves of the acanthus (*Heracleum spondylium*) by Willstätter and Isler's process (Abstr., 1911, i, 392). The separation of the two components has been effected by the partition method, the *b* compound being much less soluble in ether than the *a* compound. For practical purposes, the two partition liquids consist of 66% aqueous methyl alcohol, and a mixture of ether and petroleum, b. p. 30—50°. The method of procedure varies somewhat, according as the methylchlorophyllide mixture is rich or not in the *b* compound, but in principle the process consists in shaking the ether-petroleum solution of the methylchlorophyllides with successive quantities of 66% methyl

alcohol until the *b* compound, together with some of the *a* compound, has passed into the aqueous alcoholic layer. The ether-petroleum layer is then frequently shaken with water to remove the bulk of the ether, whereby methylchlorophyllide-*a*, which is insoluble in petroleum, is precipitated. The methylchlorophyllide-*b* is isolated from the aqueous alcoholic extracts by a somewhat complicated process, and is finally purified by the fractional precipitation of its ethereal solution by petroleum and talc.

Methylchlorophyllide-a, $C_{32}H_{30}ON_4Mg(CO_2Me)_2,\frac{1}{2}H_2O$, crystallises from ether in bluish-green, rhombic leaflets, yields bluish-green solutions with red fluorescence, exhibits the "brown phase" reaction, and is converted, when quite pure, only into phytochlorin-*e* by treatment with methyl-alcoholic potassium hydroxide under definite conditions. *Methylchlorophyllide*-b, $C_{32}H_{28}O_2N_4Mg(CO_2Me)_2,\frac{1}{2}H_2O$, crystallises in olive-green or brown, rhombic plates, and forms in absolute alcohol a greenish-yellow solution with brownish-red fluorescence, is more stable than the *a* compound towards dilute hydrochloric acid, develops in the phase tests initially a red coloration which changes to brownish-red and finally to yellowish-green, and yields phytorhodin-*g* by proper treatment with methyl-alcoholic potassium hydroxide.

The enzymatic hydrolysis of chlorophyll by chlorophyllase yields a mixture of the free chlorophyllides *a* and *b*; the hydrolysis is effected best by extracting fresh leaves (of *Heracleum* or *Stachys*) with 60—80% aqueous acetone (also the enzymatic hydrolysis of the preceding methylchlorophyllides *a* and *b* in aqueous acetone yields the corresponding free chlorophyllides; the process, however, is more difficult than is the case with crude chlorophyll). The separation of the chlorophyllides *a* and *b* is effected, as in the case of the methyl esters, by the partition method with aqueous methyl alcohol and ether-petroleum. *Chlorophyllide*-a, $CO_2H\cdot C_{32}H_{30}ON_4Mg\cdot CO_2Me,\frac{1}{2}H_2O$, crystallises from aqueous ether or acetone in six-sided plates, which are bluish-black by reflected and green to bluish-green by transmitted light. Its solutions are bluish-green with red fluorescence. By treatment with dry ammonia, the substance absorbs $2NH_3$, one of which is easily lost, the other only with difficulty. In consequence of its acid nature, chlorophyllide-*a* is extracted from its ethereal solution by *N*/1000-potassium hydroxide. The separation of chlorophyllide from alkylchlorophyllides is conveniently effected by leading ammonia into the ethereal solution, whereby the former is precipitated as the ammonium salt. By prolonged warming in a vacuum or by keeping in the solid state or in dilute solution, the chlorophyllide changes to magnesium phæophorbide, which is insoluble in ether. *Chlorophyllide*-b, $CO_2H\cdot C_{32}H_{28}O_2N_4Mg\cdot CO_2Me$, crystallises from acetone in yellow to olive-green, six-sided leaflets, forms yellowish-green solutions with brownish-red fluorescence, absorbs $2NH_3$, one of which is retained even in a vacuum, and is more strongly acidic than the *a* compound, being extracted from ethereal solution by *N*/2000-potassium hydroxide.

Methylchlorophyllide-*a* is easily and quantitatively converted into *methylphaeophorbide*-a by treating its ethereal solution with 10% hydrochloric acid for two minutes; the pure, crystalline methylphæophorbide-*a* is then obtained by concentrating the ethereal

solution. In a similar manner, methylchlorophyllide-*b* is converted into *methylphaeophorbide* b by 15% hydrochloric acid. On account of their difference in basicity, mixtures of methylphæophorbides *a* and *b* are separated much more conveniently by hydrochloric acid than by the partition method. The *a* compound is extracted completely from its ethereal solution by 18% hydrochloric acid, whilst the *b* compound requires the use of 23% acid. The ethylphæophorbides *a* and *b* (Abstr., 1911, i, 659) can be separated in a similar manner. *Methylphaeophorbide*-a, $C_{32}H_{32}ON_4(CO_2Me)_2$, crystallises in rhombic leaflets or twinned prisms, which have a violet-black lustre, appear brownish-yellow or brownish-red under the microscope, and form a dark violet powder. The ester dissolves in formic or hydrochloric acid with a blue colour, and in ether or other indifferent solvents with an olive-green colour, similar to that of phytochlorin-*e*, but differing by exhibiting a red fluorescence. Methylphæophorbide-*a* has acid number 16. When heated slowly it softens at about 150° and has m. p. 210—220° (decomp.); at 220° it still yields mainly phytochlorin-*e* after hydrolysis. *Methylphaeophorbide*-b, $C_{32}H_{30}O_2N_4(CO_2Me)_2$, forms large, olive-green or brown, rhombic crystals, and yields a reddish-brown, fluorescent solution in ether and a green solution in hydrochloric acid. The ester, which has acid number 21, softens at 200° and begins to decompose at about 250°; after being heated at this temperature it still yields nearly pure phytorhodin-*g* by hydrolysis with potassium hydroxide.

Excluding phytochlorin-*e* and phytorhodin-*g*, the free phæophorbides *a* and *b* are the most easily obtainable chlorophyll derivatives. They can be prepared by three methods: (1) By shaking an ethereal solution of the chlorophyllides *a* and *b* with 16% hydrochloric acid, the magnesium compounds are decomposed and the phæophorbide-*a* passes entirely into the acid solution, the *b* compound remaining in the ethereal layer; (2) an ethereal solution of the methylchlorophyllides *a* and *b* is treated for two hours with 25% hydrochloric acid, whereby the magnesium compounds are decomposed and the carbomethoxy-group *a* is hydrolysed. The mixture of phæophorbides *a* and *b* is then isolated, and is separated as in method (1). The best process is (3), in which phæophytin (phytylphæophorbide *a* and *b*) in ethereal solution is treated with 34—35% hydrochloric acid for three-quarters tc one hour. The solution is diluted with water, the phytol removed by ether, and the solution is further diluted with water; the phæophorbides are extracted by an excess of ether, and the ethereal solution is concentrated and treated with 16% hydrochloric acid, whereby phæophorbide *a* is removed.

Phaeophorbide-a, $CO_2H{\cdot}C_{32}H_{32}ON_4{\cdot}CO_2Me$, crystallises in bluish-black, rhombic plates, which appear olive-green or olive-brown under the microscope. The colours of its solutions in different solvents are like those of methylphæophorbide-*a*. The substance absorbs $2NH_3$, one of which is lost only in a vacuum. The acid number is 15. Phæophorbide-*a* is extracted from its ethereal solution by *N*/100-ammonia or potassium hydroxide, by 0·1% sodium carbonate, and by 1% sodium hydrogen carbonate or phosphate. *Phaeophorbide*-b, $CO_2H{\cdot}C_{32}H_{30}O_2N_4{\cdot}CO_2Me$, crystallises from ether in small, rhombic

plates and needles, which appear olive-green or brown under the microscope. The substance absorbs approximately $2NH_3$, which is almost entirely lost at the ordinary pressure. It forms a reddish-brown, fluorescent solution in ether, and a green solution, in hydrochloric acid. Phæophorbide-*b* is more acidic than the *a* compound; its acid number is 19—20, and it is extracted from ethereal solution by 0·2% sodium hydrogen carbonate or by 0·25% disodium hydrogen phosphate. By treatment with methyl-alcoholic potassium hydroxide it gives a "red phase."

The term "allomerism" is employed to denote the changes which the chlorophyllides and the alkylchlorophyllides undergo in alcoholic solution (Abstr., 1911, i, 660). Allomerism in alcoholic solution is catalytically accelerated by the presence of glass, but not of platinum or silver; it is prevented by the presence of a trace of acid. Allomeric changes are to be explained probably by the rupture of the lactam group in the chlorophyll derivative, and the formation of a new lactam group.

The degradation of chlorophyll (for example, chlorophyll-*a*, annexed formula) can now be effected in three ways, in each of which the reagent attacks the chlorophyll molecule at a different point.

$$\overset{\beta}{CO_2Me}\cdot[\overbrace{C_{31}H_{29}N_3Mg}^{\overset{\gamma}{NH}-\overset{\gamma}{CO}}]\cdot\overset{\alpha}{CO_2\cdot C_{20}H_{39}}$$

(1) By the enzymatic action of chlorophyllase, changes only occur at the *a*-group; in methyl or ethyl alcohol the phytyl group is replaced by methyl or ethyl, whilst in aqueous acetone it is replaced by hydrogen, this being the only method by which the free chlorophyllides can be obtained. (2) By gentle treatment with acids, the magnesium is replaced by hydrogen and phæophytin is obtained. By more energetic treatment, hydrolysis occurs at the *a*-group, and the free phæophorides are produced; since these still exhibit the "brown phase," the γ-lactam group is still intact. (3) Alkalis first attack the γ-lactam group in the "brown phase"; subsequently a new lactam group is formed. Then follows hydrolysis at the *a*-group, and, finally, with difficulty at the β-group. At higher temperatures, alkalis cause an elimination of carbon dioxide, and degradation to di- and mono-basic phyllins and porphyrins ensues. A diagrammatic representation of these changes is given.

The formulæ of the compounds in this paper are to replace those previously recorded (Abstr., 1911, i, 659). C. S.

Phylloporphyrins. LEON MARCHLEWSKI (*Annalen*, 1912, 388, 63—65).—Willstätter and Fritzsche (Abstr., 1910, i, 136) state that Schunck and Marchlewski's phylloporphyrin is a mixture of two substances of different basicity. The author, therefore, has heated *allo*phyllotaonin (Abstr., 1907, i, 866) with 10% alcoholic potassium hydroxide at 200°, whereby only Schunck and Marchlewski's phylloporphyrin together with feebly basic by-products is obtained. Chlorophyllanic acid, however, by the same treatment, yields two markedly basic products, which are separated by 0·25% hydrochloric acid. One of these products, called phylloporphyrin-*a*, is identical

with Schunck and Marchlewski's phylloporphyrin; the other more basic product is called phylloporphyrin-β. By treatment with alcoholic potassium hydroxide at 200°, phyllocyanin and *allo*chlorophyllanic acid each yield mainly phylloporphyrin-β, very little of the α-compound being produced (compare following abstracts). C. S.

The Chlorophyll Group. XII. β-Phylloporphyrin. LEON MARCHLEWSKI and J. ROBEL (*Biochem. Zeitsch.*, 1912, **39**, 6—11; *Bull. Acad. Sci. Cracow*, 1912, *A*, 41—46).—The authors believe that the so-called pyrroporphyrin of Willstätter and Fritzsche is essentially the phylloporphyrin of Schunck and Marchlewski, which had not been sufficiently purified, in that the former investigators had underestimated the basicity of the less basic product in the mixture. When these porphyrins are prepared from crude chlorophyllanic acid (from maple chlorophyll) by the method described in detail by the authors, two products are formed simultaneously, namely, a strongly basic β-phylloporphyrin, which can be dissolved out from its solution in ether by $\frac{1}{4}$% hydrochloric acid, and the phylloporphyrin of Schunck and Marchlewski. If $\frac{1}{2}$% acid be used instead, appreciable quantities of the last-named porphyrin are also dissolved. A comparison of the spectra of the two substances is given. S. B. S.

The Chlorophyll Group. XIII. Porphyrins from Phyllocyanin and Phylloxanthin. LEON MARCHLEWSKI and B. ŻURKOWSKI (*Biochem. Zeitsch.*, 1912, **39**, 59—63).—In view of the possibility of separating α- and β-phylloporphyrins (see Marchlewski and Robel, preceding abstract), investigations were made with the object of finding the parent substance of these two derivatives. The β-derivative is not obtained at all from the phyllotaonin of Schunck and Marchlewski, or from the pure *allo*phyllotaonin of Marchlewski and Robel. These yield the α-substance. On the other hand, phyllocyanin and phylloxanthin, which stand in near relationship to *neo*chlorophyll and *allo*chlorophyll, yield chiefly the β-derivative. The previously-expressed views on the subject are not correct, owing at the time to the want of a satisfactory method for separating the two porphyrins. The experimental details of the method of preparing the β-substance from phyllocyanin and phylloxanthin are given in full. S. B. S.

The Red and Blue Pigments of the Algæ. HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1912, **76**, 396—425. Compare Abstr., 1910, i, 866).—The occurrence of phycoerythrin and phycocyanin in a number of varieties of *Florideæ* and *Cyanophyceæ* has been investigated.

In addition to the properties previously given (*loc. cit.*), phycoerythrin crystallises in hexagonal prisms usually without pyramidal faces; these are optically negative. The same modification has been isolated from twenty species of *Florideæ*; from three species, *Polysiphonia Brodiæi*, *P. nigrescens*, and *Rhodomela subfusca*, a modification was obtained which lacked the fluorescent properties. So far, phycoerythrin has only been obtained from the *Florideæ*.

Three modifications of phycocyanin have been identified.

Bluish-green phycocyanin shows a remarkable dark carmine-red fluorescence, and has an absorption band in the orange between C and D

with a maximum at $\lambda = 624$—618. It crystallises in hexagonal rhombohedra.

Blue phycocyanin also gives a splendid dark carmine-red fluorescence, and has two absorption bands, one in the orange between C and D with a maximum at $\lambda = 615$—610, and the other in the yellow-green between D and E, but nearer to D, with a maximum at $\lambda = 577$—573; it was not obtained crystalline. This modification is widely distributed amongst the *Cyanophyceae*.

Bluish-violet phycocyanin has the same fluorescence, and shows absorption bands in the orange between C and D with a maximum at $\lambda =$ 618—613, and in the green between D and E, but nearer E, with the maximum at $\lambda = 553$—549. It crystallises in rhombic plates, which are blue across the shorter diagonal, violet across the longer. This modification occurs in *Ceramium rubrum*.

Phycocyanin is characteristic of the *Cyanophyceæ*, but occurs in a few *Florideæ*. E. F. A.

Melanin. ROSS AIKEN GORTNER (*Biochem. Bulletin*, 1911, 1, 207—215. Compare Abstr., 1911, ii, 908).—Melanins are probably formed by the interaction of an oxydase and an oxydisable chromogen. They differ in solubility in dilute acids; those which are soluble contain a protein complex; those which are insoluble are the granules seen in hairs and tissues. Tyrosine, lysine, and arginine are obtained as hydrolytic products from the former class (melano-proteins).

W. D. H.

Formation of Gallamide from Acetyltannin. MAXIMILIAN NIERENSTEIN (*Ber.*, 1912, **45**, 533—534. Compare Abstr., 1910, i, 487).—The formation of gallamide from acetyltannin by heating with alcoholic ammonia is regarded as doubtful; the former analytical values were calculated incorrectly. E. F. A.

Hydroxyhydrofurans. GEORGES DUPONT (*Compt. rend.*, 1912, **154**, 599—601. Compare Abstr., 1911, i, 554, 804).—Ketohydrofurans are not reduced by zinc and alkalis, by sodium amalgam, or by hydrogen in presence of platinum. Sodium ethoxide at 120°, however, gives red compounds, which on treatment with water yield the corresponding hydroxyhydrofurans, together with viscous, high-boiling liquids.

3-Hydroxy-2:2:5:5-tetramethyltetrahydrofuran, $\begin{matrix} OH\cdot CH\cdot CMe_2 \\ | \\ CH_2\cdot CMe_2 \end{matrix}\!\!>\!O$, has b. p. 84°/15 mm., D^{17} 0·9483, n_D 1·4435; the *acetate* has b. p. 181—182°, D^{15} 0·9587, n_D 1·4256, and the *acid phthalate*, m. p. 139—141°. *3-Hydroxy-2:5-dimethyl-2:5-diethyltetrahydrofuran* has b. p. 107°/19 mm., D^{15} 0·9539, n_D 1·4547; the *acetate* has b. p. 97—98°/15 mm., D^{15} 0·9589, n_D 1·4382.

Ketodimethylhydrofuran reacts with organo-magnesium halides, giving derivatives of hydroxyhydrofurans, whereas the ketotetra-alkylhydrofurans react in the enolic form, yielding hydrocarbons. The following compounds have been obtained:

3-Hydroxy-2:3:5-trimethyltetrahydrofuran, b. p. 71—73°/16 mm.,

171—173°/755 mm., D^{21} 0·9719, n_D 1·4420; *3-hydroxy-2:5-dimethyl-3-ethyltetrahydrofuran*, b. p. 79—81°/16 mm., D^{21} 0·9693, n_D 1·4485; *3-hydroxy-3-phenyl-2:5-dimethyltetrahydrofuran*, b. p. 138—140°/16 mm., D^{20} 1·0827, n_D 1·5310; *3-hydroxy-3-benzyl-2:5-dimethyltetrahydrofuran*, b. p. 146—147°/15 mm., D^{15} 1·0598, n_D 1·5251; *3-hydroxy-3-p-tolyl-2:5-dimethyltetrahydrofuran*, b. p. 149—150°/15 mm., D^{15} 1·0456, n_D 1·5288; *3-hydroxy-3-benzyl-2:2:5:5-tetramethyltetrahydrofuran*, m. p. 89°.

W. O. W.

Action of Sodium Hydroxide on 5-Methylfurfuraldehyde. JAN J. BLANKSMA (*Chem. Weekblad*, 1912, **9**, 186—187).—Sodium hydroxide converts 5-methylfurfuraldehyde into the corresponding alcohol, *5-methyl-2-hydroxymethylfuran*, and acid, 5-methylpyromucic acid. The alcohol is a colourless, mobile liquid of fruit-like odour. It has b. p. 100°/11 mm. Exposure to light and air converts it into a yellow syrup, which gradually becomes brown and viscous, and ultimately changes to a dark-coloured resin.

A. J. W.

Synthesis of Pyromeconic Acid. ALBERTO PERATONER (*Gazzetta*, 1911, **41**, ii, 686—697).—The author has effected the synthesis of pyromeconic acid by direct oxidation of 4-pyrone, after unsuccessful attempts to obtain derivatives of meconic acid from the substance $CO_2Et{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH(OEt){\cdot}CO{\cdot}CO_2Et$ by dehydration.

When ethyl acetol ether is condensed with one molecule of ethyl oxalate in the presence of sodium ethoxide, the vessel being cooled externally with ice, and the solvent subsequently evaporated in a vacuum below 40°, a *sodium* salt is produced, which, on treatment with concentrated acetic acid and distillation in a vacuum, yields *ethyl α-ethoxybutane-βδ-dione-δ-carboxylate*,

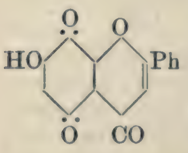
$$OEt{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et,$$

which is a slightly yellow oil, b. p. 135—140°/20 mm. Its aqueous solution gives a cherry-red coloration with ferric chloride, and with *copper* acetate it yields a green salt, $C_{18}H_{26}O_{10}Cu$. By the action of a second molecule of ethyl oxalate on the sodium salt above described, and proceeding as suggested by Willstätter and Pummerer in the case of xanthochelidonic acid (Abstr., 1904, i, 1043), *diethyl β-ethoxypentane-αγε-trione-αε-dicarboxylate*, $CO_2Et{\cdot}CO{\cdot}CH(OEt){\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et$, is obtained. The triketone is purified by sublimation at 20 mm., treatment with water and resublimation, and then forms colourless, acicular crystals or scales, m. p. 124—125°. With alkalis it yields yellow, amorphous *xantho*-salts, but with ferric chloride it gives a dirty green coloration which becomes reddish-brown, whilst copper acetate yields a green *copper* salt. It was not found possible to eliminate the elements of water from the triketone in any way, but when it is boiled for half an hour with hydriodic acid (D 1·7) *n*-pimelic acid is produced.

Pyromeconic acid is formed when one molecule of hydrogen peroxide (3% solution) is added slowly to a solution of one molecule of 4-pyrone, one molecule of ferrous sulphate, and sulphuric acid, the mixture being cooled in ice. The isolation of the acid may be effected either by treating the liquid at its boiling point with ammonia and air until the

pyrone is converted into pyridone and the iron is precipitated, or by prolonged extraction of the liquid with chloroform, the product in either case being purified by sublimation in a vacuum below 100° and by recrystallisation. R. V. S.

Anthocyanins. II. An Anthocyanin-like Oxidation Product of Chrysin. MAXIMILIAN NIERENSTEIN (*Ber.*, 1912, **45**, 499—501. Compare this vol., i, 42).—By oxidation with chromic and acetic acids in the cold, chrysin yields *chrysone* (annexed formula), m. p. above 360°, dark red needles. It exhibits the blue and the red colour reactions of anthocyanin with alkalis and concentrated sulphuric acid respectively. It forms an *acetyl* derivative, $C_{17}H_{10}O_6$, m. p. 324—326° (decomp.), red needles, and when heated with acetic anhydride and zinc dust yields an acetylated hydroxychrysin, by the hydrolysis of which 1 : 3 : 4-*trihydroxyflavone*, m. p. 304—305°, is obtained (*triacetyl* derivative, m. p. 214—217°, colourless needles).



Fisetin is not oxidised by chromic and acetic acids. C. S.

Some Derivatives of Hydroxyquinol. VII. GUIDO BARGELLINI and ERMANNO MARTEGIANI (*Gazzetta*, 1911, **41**, ii, 612—618).—The paper deals with two coumarins obtained by condensation of hydroxyquinol with ethyl acetoacetate and ethyl benzoylacetate respectively. When hydroxyquinol triacetate and ethyl acetoacetate are heated together for half an hour on the water-bath with 73% sulphuric acid, β-methylæsculetin is obtained, identical with that prepared by von Pechmann and von Krafft (Abstr., 1901, i, 285). Its *diacetyl* derivative, $C_{14}H_{12}O_6$, has m. p. 149—151°; it dissolves in concentrated sulphuric acid, giving a yellowish-green coloration. The *dibenzoyl* derivative, $C_{24}H_{16}O_6$, crystallises in colourless needles, m. p. 152°; it dissolves in concentrated sulphuric acid, giving a slight yellow coloration. The *dimethyl ether* crystallises in colourless needles, m. p. 130—134°. The *monomethyl ether*, $C_{11}H_{10}O_4$, formed in its preparation, crystallises in slightly yellow needles, m. p. 173—175°.

β-Phenylaesculetin, $C_{15}H_{10}O_4$, is a yellow, crystalline powder, obtained by condensation of hydroxyquinol triacetate with ethyl benzoylacetate in the presence of 73% sulphuric acid. It dissolves in concentrated sulphuric acid, giving a yellow coloration, and with ferric chloride in alcoholic solution it gives a green coloration. The *diacetyl* derivative, $C_{19}H_{14}O_6$, crystallises in colourless needles, m. p. 156°. The *benzoyl* derivative crystallises in colourless needles, m. p. 162—164°. The dimethyl ether was not obtained in crystalline form, but crystals of a substance, m. p. 122—124°, were obtained, which was probably the *monomethyl ether*. R. V. S.

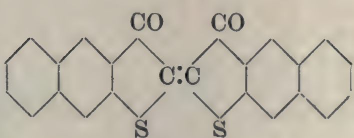
New Method for the Preparation of Thiophen. WILHELM STEINKOPF (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 220—221).—Acetylene is passed through an iron tube containing pyrites at a temperature of 300°. The tube is provided with a transporting screw for the removal of spent pyrites. The liquid

product obtained in the condensing vessel contains 40% of thiophen. In seven or eight hours, 800 grams of distillate may be obtained, using 8 kilograms of pyrites. The thiophen is easily obtained with a purity of 95—96%, the impurities being sulphur compounds with traces of benzene. Larger quantities of benzene are not obtained in the process. The remainder of the distillate is a complex mixture, from which only a single compound, $C_4H_6S_3$, b. p. 36—38°, with a very penetrating odour of garlic, has been isolated. C. H. D.

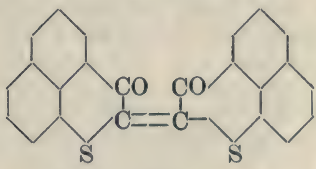
s-Dioxythionaphthen. Maurice Lanfry (*Compt. rend.*, 1912, **154**, 519—521. Compare Abstr., 1911, i, 555, 740, 1009).—s-*Dioxythionaphthen*, $C_8H_6O_2S$, is prepared by the action of hydrogen peroxide on thionaphthen (Gattermann, Abstr., 1894, i, 92), employing 0·5—0·8 gram of active oxygen per gram of thionaphthen. The compound crystallises in colourless needles, m. p. 142—143°; it does not give the Laubenheimer reaction, and does not show the properties of a phenol, a ketone, or a quinone. It follows, therefore, that the oxygen is attached directly to sulphur, as indicated by the name the author suggests for the compound.

Dioxythionaphthen unites with bromine to form a *dibromide*, $C_8H_6O_2SBr_2$, occurring in slender needles, m. p. 168—170°. When treated with fuming nitric acid, it yields a *mononitro*-derivative, $C_8H_5O_2S\cdot NO_2$, crystallising in yellow rhombohedra, m. p. 187—188°. W. O. W.

"Thio-indigo" Dyes of the Naphthalene Series. Paul Friedländer and N. Woroshzow (*Annalen*, 1912, **388**, 1—23).—The series of reactions whereby anthranilic acid has been converted into "thio-indigo" (Abstr., 1906, i, 378; 1907, i, 334), is applicable in the naphthalene series to the preparation of "*bis*-2 : 3-*naphthathiophen-indigo*" [*bis*-2 : 3-*naphthathiophen*] and *bis*-1 : 8-*naphthapenthiophen-indigo*" [*bis*-1 : 8-*naphthathiophen*] (formulæ I and II respectively).



(I.)



(II.)

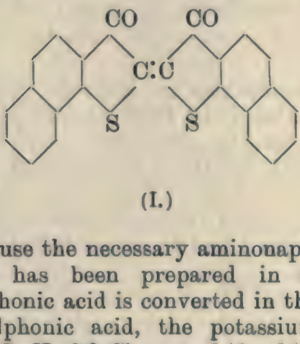
[With E. Eckstein.]—The sodium salt which is precipitated by the addition of sodium chloride to the not too dilute, diazotised solution of 2-amino-3-naphthoic acid is added to a hot solution of potassium xanthate. When the oil which separates has become solid, it is dissolved in sodium hydroxide and warmed with chloroacetic acid. By acidification, *β-3-carboxynaphthylthiolacetic acid*,

$$CO_2H\cdot C_{10}H_6\cdot S\cdot CH_2\cdot CO_2H,$$

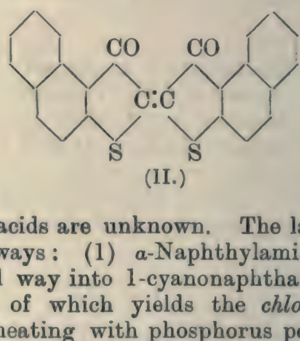
m. p. 224° (decomp.), white needles, is obtained. Its sodium salt is boiled with acetic anhydride and sodium acetate, the resulting acetoxynaphthathiophen is hydrolysed by dilute sodium hydroxide,

and the hydroxynaphthathiophen is oxidised by alkaline potassium ferricyanide, whereby *bis*-2 : 3-*naphthathiophen* is obtained. The dye crystallises in almost black needles, sublimes without decomposition, yields an orange-red vat with alkaline hyposulphite, and develops an olive-green coloration with fuming sulphuric or chlorosulphonic acid. Naphthastyril (Abstr., 1910, i, 201) is converted by boiling 10% sodium hydroxide into sodium 8-amino-1-naphthoate, the diazotised solution of which is converted by reactions similar to the preceding into *bis*-1 : 8-*naphthapenthiophen*, which crystallises in long needles with a copper lustre and sublimes with decomposition. The intermediate products isolated in its preparation are the *anhydride* of 8-thiol-1-naphthoic acid, $C_{10}H_6<\overset{S}{\underset{CO}{|}}$, m. p. 144·5—145·5°, yellow needles, *a*-8-*carboxynaphthylthiolacetic acid*, $CO_2H \cdot C_{10}H_6 \cdot S \cdot CH_2 \cdot CO_2H$, m. p. 177°, and *hydroxy*-1 : 8-*naphthapenthiophen*, $C_{10}H_6<\substack{C(OH)\\S}>CH$, m. p. 84·5—85·5°, yellow prisms (*acetyl* derivative, m. p. 130·5°, yellow leaflets), which is oxidised to the dye best by atmospheric oxygen.

"*Bis*-1 : 2-*naphthathiophenindigo*" [*bis*-1 : 2-*naphthathiophen*] and *bis*-2 : 1-*naphthathiophen* [*bis*-2 : 1-*naphthathiophen*] (formulæ I and II respectively) cannot be prepared by the preceding method,



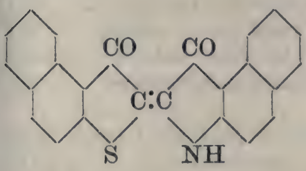
(I.)



(II.)

because the necessary aminonaphthoic acids are unknown. The latter dye has been prepared in three ways: (1) *a*-Naphthylamine-2-sulphonic acid is converted in the usual way into 1-cyanonaphthalene-2-sulphonic acid, the potassium salt of which yields the *chloride*, $CN \cdot C_{10}H_6 \cdot SO_2Cl$, m. p. 141—142°, by heating with phosphorus pentachloride. The chloride is reduced by zinc and hydrochloric acid to the mercaptan, which reacts with sodium chloroacetate in alkaline solution to form, after acidification, *β*-1-*carboxynaphthylthiolacetic acid*, $CO_2H \cdot C_{10}H_6 \cdot S \cdot CH_2 \cdot CO_2H,H_2O$, m. p. 69° (134·5° when anhydrous), colourless needles. By prolonged boiling with concentrated sodium hydroxide and acidification of the hot solution, this acid yields *hydroxy*-2 : 1-*naphthathiophen*, $C_{10}H_6<\substack{C(OH)\\S}>CH$, m. p. 121°, colourless needles, which reacts with benzaldehyde and *p*-nitrobenzaldehyde to form the *thioindogenides*, $C_{10}H_6<\substack{CO\\S}>C:CHPh$, m. p. 159°, yellow needles, and $C_{10}H_6<\substack{CO\\S}>C:CH \cdot C_6H_4 \cdot NO_2$, m. p. 287°, yellow needles, respectively, and with *β*-naphthisatin chloride in hot xylene to form

naphthindole-2 : 1-naphthathiophen (annexed formula), dark violet



crystals, which develops a bluish-violet coloration in concentrated sulphuric acid. (2) 2-Thiol-α-naphthylamine and potassium chloroacetate are heated with concentrated potassium hydroxide, whereby, after acidification, the *lactam* of β-1-aminonaphthylthiolacetic acid, $C_{10}H_6<\begin{matrix}NH\cdot CO \\ S—CH_2\end{matrix}$, m. p. 203°, is obtained. *β-1-Cyanonaphthylthiolacetic acid,*

$CN\cdot C_{10}H_6\cdot S\cdot CH_2\cdot CO_2H$,

m. p. 173°, which is prepared from the preceding compound, is converted by hot potassium hydroxide into *potassium 3-aminonaphthathiophen-2-carboxylate,* an acidified solution of which yields hydroxy-2 : 1-naphthathiophen by boiling. (3) *β-Naphthylthiolacetic acid,* $C_{10}H_7\cdot S\cdot CH_2\cdot CO_2H$, m. p. 91°, obtained by heating β-naphthyl mercaptan and chloroacetic acid in alkaline solution, is converted directly into hydroxy-2 : 1-naphthathiophen by 10% chlorosulphuric acid in chloroform at the ordinary temperature.

Bis-2 : 1-naphthathiophen, which is obtained by the oxidation of hydroxy-2 : 1-naphthathiophen, best by alkaline potassium ferricyanide, crystallises in reddish-brown needles with a bronze lustre, develops a dark blue coloration with concentrated sulphuric acid, and yields a yellow vat with alkaline hyposulphite.

Bis-1 : 2-naphthathiophen, which can be obtained by methods analogous to the preceding, forms dark red needles, develops a brownish-red coloration with concentrated and an intense blue with fuming sulphuric acid, and yields a yellow vat. The *lactam* of α-2-aminonaphthylthiolacetic acid, $C_{10}H_6<\begin{matrix}S—CH_2 \\ NH\cdot CO\end{matrix}$, m. p. 210°, *α-2-cyanonaphthylthiolacetic acid,* $CN\cdot C_{10}H_6\cdot S\cdot CH_2\cdot CO_2H$, m. p. 137—138°, and *hydroxy-1 : 2-naphthathiophen,* $C_{10}H_6<\begin{matrix}C(OH) \\ S\end{matrix}>CH$, m. p. 142° (*benzylidene* derivative, m. p. 181°, yellow leaflets), are also described.

C. S.

Organic Syntheses by means of Sunlight. VII. Photosynthesis of a New Alkaloid from Acetophenone and Ammonia. EMANUELE PATERNÒ and CONCETTO MASELLI (*Gazzetta,* 1912, 42, i, 65—75; *Atti R. Accad. Lincei,* 1912, [v], 21, i, 235—243).—When acetophenone dissolved in saturated alcoholic ammonia is exposed to sunlight for several months, a substance is produced which, from its properties, is to be regarded as an alkaloid. The yield does not exceed 20%. The new *alkaloid,* $C_{18}H_{18}N_2$, forms large, transparent crystals [ZAMBONINI: the crystals belong to the triclinic system: $a:b:c = 1\cdot5017:1:1\cdot5993$; α 91° 21·5′, β 106° 14′, γ 79° 50′], which have m. p. 227° and dissolve in alcohol, giving a strongly alkaline solution. The substance has about the normal molecular weight in freezing acetic acid. The *nitrate* is a white, crystalline powder, m. p. 258°. The *hydrochloride,* $C_{18}H_{18}N_2,HCl$,

crystallises in tufts of long, colourless needles, and does not change when heated in a current of dry hydrogen chloride in a bath at 350°. The *platinichloride*, $(C_{18}H_{18}N_2)_2,H_2PtCl_6$, forms silky, flesh-coloured laminæ, which begin to blacken at 260°. The *silver* salt is a white, amorphous powder. The base yields a *mononitroso*-derivative,

$$C_{18}H_{17}N_2{\cdot}NO,$$

when warmed with potassium nitrite in solution in glacial acetic acid and alcohol; the substance crystallises in lustrous laminæ, m. p. 218° (decomp.).

Negative results were obtained in attempts to oxidise the alkaloid with permanganate and to determine its alkyloxy-groups. When the substance is heated in a sealed tube for three hours at 370°, a portion of it is converted into a reddish-brown oil, but the greater part remains unchanged. When the alkaloid was heated with hydriodic acid and phosphorus for six days, the product consisted of the *hydriodide* of the base, together with a small quantity of a yellow oil. R. V. S.

Rearrangement of Cinchonine and Quinine into Their Poisonous Isomerides Cinchotoxine and Quinotoxine. HENRY C. BIDDLE (*Ber.*, 1912, **45**, 526—528. Compare Rabe, 1911, ii, 33).—Salts of cinchonine and quinine when heated at 95—98° in aqueous solution with or without excess of acid undergo rearrangement into their poisonous isomerides cinchotoxine and quinotoxine. The velocity of the reaction is increased when the dissociation constant of the acid used is lessened; this applies to the action of acids both on salts and on free alkaloid. With acetic or propionic acid the change is practically complete after forty-eight hours' heating; under the same conditions, using an excess of hydrochloric acid, practically no rearrangement takes place. The same change also takes place slowly when the salts are heated at 36°, or when the salt solutions are exposed to direct sunlight at the ordinary temperature; in this case much resinous matter is also formed, which colours the solution brown.

It is possible that cinchotoxine and quinotoxine are formed similarly in the human organism. E. F. A.

The Symmetry of Sparteine. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1912, **154**, 309—312. Compare this vol., i, 210).—The action of methyl iodide on *iso*sparteine hydriodide at 135° leads to the formation of *iso*sparteine α-methiodide. The action of methyl iodide on sparteine has already been described; since it leads to analogous results, it follows that both bases are symmetrical. As this is impossible owing to the mode of formation of *iso*sparteine, it follows that the action of methyl iodide on the hydriodides is not purely one of simple addition, but involves displacement of the halogen hydride by the alkyl iodide and direct addition of the displaced hydrogen iodide. There is therefore no absolute proof of the symmetry of the sparteine molecule.

Reasons are adduced in support of the view that stereoisomerism of the groups about the nitrogen atom is sufficient to explain the existence of two isomeric methylsparteine methiodides. W. O. W.

Methylation of Brucine. GUSTAV MOSSLER (*Monatsh.*, 1912, 33, 19—32).—*Methylbrucine acetate*, $C_{24}H_{30}O_5N_2,C_2H_4O_2,5H_2O$, prepared by the cautious addition in portions of silver acetate to a finely divided suspension of brucine methiodide in water, crystallises in rhombic plates, m. p. (anhydrous) 208—209° (decomp.), $[\alpha]_D^{20} - 9.97°$. The same substance was obtained by the action of acetic acid on methylbrucine. When warmed with hydrochloric acid, brucine methochloride is obtained.

On treatment with methyl iodide in methyl-alcoholic solution, *dimethylbrucine iodide*, $C_{25}H_{33}O_5N_2I,2\frac{1}{2}H_2O$, is obtained in flat, right-angled plates, m. p. 268° (decomp.).

Dimethylbrucine acetate, $C_{27}H_{36}O_7N_2,5H_2O$, is very similar to the monomethyl compound, m. p. 205—206°, $[\alpha]_D^{20} - 7.14°$. With hydrochloric acid the salt, $C_{25}H_{34}O_5N_2Cl_2$, is obtained, m. p. 261°.

Crystalline products could not be obtained by the oxidation of methylbrucine.

Methyl- and dimethyl-brucine are considered to have the structure of betaines, whereas dimethylbrucine iodide is a quaternary iodide.

E. F. A.

Hæmopyrrole. J. GRABOWSKI and LEON MARCHLEWSKI (*Ber.*, 1912, 45, 453—456).—The authors have subjected 2:4-dimethyl-3-ethylpyrrole (Knorr and Hess, Abstr., 1911, i, 1019) to the action of benzenediazonium chloride, and find that its behaviour differs from that of hæmopyrrole obtained from hæmin, since it yields orange needles of *benzeneazo-2:-4-dimethyl-3-ethylpyrrole hydrochloride*,

$$C_8H_{12}N\cdot N_2C_6H_5,HCl.$$

This substance has no definite m. p., but begins to decompose at 120°, and evolves gas at about 155°. Attempts to convert it into a disazo-derivative were unsuccessful. The authors draw the conclusion that trisubstituted derivatives of pyrrole are incapable of reacting with more than one molecule of a diazonium salt, and doubt the view that one $-N_2C_6H_5$ group of the hæmopyrrole derivative, $C_8H_{11}N(N_2C_6H_5)_2$, is attached to the nitrogen atom. The stability of the hæmopyrrole dyes towards hydrochloric acid and the so-called *H*-acid is a further argument against an azo-diazoamino-constitution.

The reduction of methyl-*n*-propylmaleinimide (Marchlewski and Buraczewski, Abstr., 1905, i, 399; 1906, i, 779) has been repeated with larger quantities of material. From the product of the reduction, two crystalline dyes were isolated in the form of hydrochlorides, but in quantity insufficient for analysis. In hydrochloric acid and in neutral solution, however, their spectra are identical with those of the dyes prepared from hæmopyrrole. H. W.

Syntheses of Phyllopyrrole. Chemistry of Hæmopyrrole. HANS FISCHER and E. BARTHOLOMÄUS (*Ber.*, 1912, 45, 466—471).—When substituted pyrroles are heated with alcoholic solutions of sodium methoxide or ethoxide, alkylation occurs at a carbon atom. In this manner the authors have synthesised phyllopyrrole,

$$NH<\begin{matrix}CMe:CMe\\ |\\ CMe:CEt\end{matrix}$$

(compare Willstätter and Asahina, Abstr., 1912, i, 42), from 2 : 4-dimethyl-3-ethylpyrrole and sodium methoxide, from 2 : 4 : 5-trimethylpyrrole and sodium ethoxide, and from hæmopyrrole and sodium methoxide. The highest m. p. observed for phyllopyrrole was 69°. Phyllopyrrole picrate has m. p. 104—105°.

Similarly, 2 : 4-dimethyl-3-ethylpyrrole was converted by means of sodium ethoxide into 2 : 4-dimethyl-3 : 5-diethylpyrrole.

When hæmopyrrole is heated with sodium ethoxide, it yields a dimethyldiethylpyrrole (isolated in the form of its *picrate*, m. p. 102—103°) differing from that described above. Since the relative positions of the methyl and ethyl groups in hæmopyrrole have been determined by its oxidation to methylethylmaleinimide, the authors are led to propose the formula $NH<\begin{matrix}CMe:CMe\\ \mid \\ CH-CEt\end{matrix}$ for hæmopyrrole, and regard its product of its ethylation as 2 : 3-dimethyl-4 : 5-diethylpyrrole.

By coupling 2 : 4 : 5-trimethylpyrrole with diazobenzenesulphonic acid, a red *dye*, $C_{13}H_{15}O_3N_3S$, was obtained.

The preparation of phyllopyrrole from hæmin is fully described.

H. W.

Mirror Image Isomerism with Iron Compounds. Alfred Werner (*Ber.*, 1912, 45, 433—436).—In order to show that ethylenediamine is not a necessary cause of optical activity in complex metal ammonias, the author has investigated the tri-α-dipyridylferrous compounds, $[(Dipyr)_3Fe]X_2$, and has succeeded in obtaining the optically active lævo-isomerides by means of *d*-ammonium tartrate. The observed specific rotations are very great (>500°), but racemisation takes place very quickly in aqueous solution, the rotation falling to half its original value in half-an-hour.

The compounds obtained belong to the class of molecular asymmetry II (this vol., i, 166); they prove that optical activity does not depend on the presence of ethylenediamine, and also, that it can occur with co-ordination compounds of a divalent element.

Tri-α-dipyridylferrous bromide was prepared in a manner described previously (Blau, Abstr., 1889, 1212; 1899, i, 387), and resolved as follows: 2·5 grams were dissolved in 112 c.c. of water and 60 grams of *d*-ammonium tartrate added to the filtered solution, which was then cooled to −4°. After some time, intense red crystals of l-*tri-α-dipyridylferrous*-d-*tartrate* separate, which cannot be recrystallised without loss of activity. A 0·125% solution gave α −0·35° in a decimetre tube at 15°; after three and a-half hours the rotation had fallen to zero.

l-*Tri-α-dipyridylferrous bromide*, $[Fe(Dipyr)_3]Br_2,6H_2O$, was obtained from the tartrate by double decomposition with potassium bromide; it could not be recrystallised, owing to rapid racemisation. It forms dark red, flat crystals, and has [α] −520° and [M] −4117·8°, although these values are probably too low, because of racemisation. The *iodide*, $[Fe(Dipyr)_3]I_2,5H_2O$, was similarly prepared from the tartrate and sodium iodide, and forms glistening, dark red, flat leaflets; it has [α] −440° and [M] −3818·7°.

T. S. P.

The Preparation of Nitropyridine. FRANZ FRIEDL (*Ber.*, 1912, **45**, 428—430).—The direct nitration of pyridine has been accomplished by gradually adding potassium nitrate to a solution of pyridine in 18% fuming sulphuric acid heated at 330°. *β-Nitropyridine* crystallises in long, colourless needles, m. p. 41°, b. p. 216°. *β-Nitropyridine nitrate* has m. p. 150—151°.

The position of the nitro-group in the molecule was determined by reducing nitropyridine by means of stannous chloride to β-aminopyridine (Pollak, Abstr., 1895, i, 391), and, further, by the transformation of this compound into β-hydroxypyridine (Fischer and Renouf, Abstr., 1884, 1370).

Nitropyridine is also formed in small quantity by the action of concentrated nitric acid on a solution of pyridine in fuming sulphuric acid at 330° and atmospheric pressure. H. W.

4-Oxypyrone and Some of its Derivatives. ALBERTO PERATONER (*Gazzetta*, 1911, **41**, ii, 619—685. Compare Ost, Abstr., 1879, 708; 1882, 601; 1883, 791; 1884, 1302; 1885, 48; Peratoner, Abstr., 1902, i, 421, 493; Peratoner and others, Abstr., 1905, i, 806, 807; Palazzo, Abstr., 1905, i, 458; Palazzo and Onorato, Abstr., 1905, i, 459).—The paper deals with Ost's nitrosopyromeconic acid, and with some of its transformation products and their derivatives. The author discusses fully the constitution of the substances concerned, in the light of the previous work of himself and others and of the new experimental data now obtained.

Further details are given as to the preparation of Ost's nitrosodipyromeconic acid by the action of ethyl nitrite on pyromeconic acid. The author also finds that phenol, catechol, resorcinol, pyrogallol, α-naphthol, and thymol yield traces of the corresponding nitroso-derivatives when they are treated with alkyl nitrites at a low temperature. Benzoylacetone and ethyl benzoylacetate yield nitroso-derivatives in this way at the ordinary temperature.

When nitrosodipyromeconic acid, $C_5H_3O_4N,C_5H_4O_3$, is treated with rather more than two molecules of phenylhydrazine in glacial acetic acid, two products are obtained: (1) a *substance* crystallising in yellow needles, m. p. 165°; (2) a greyish-white, crystalline *substance*, which by treatment with hot benzene is converted into a *substance* crystallising in yellow needles, m. p. 199—200°. Both compounds have the composition required by the formula: $\begin{array}{l}\text{O·C(N:OH)·C:N·NHPh} \\ \text{CH:CH}\text{——}\text{C:N·NHPh}\end{array}$, and are to be regarded as stereoisomerides. Both yield the same *osotetrazone*, $C_{17}H_{13}O_2N_5$, when treated with warm alcoholic ferric chloride solution. The osotetrazone crystallises in red needles, m. p. 137—138°, which appear black with a metallic lustre when viewed by reflected light. Both hydrazo-oximes when kept at 210° lose one molecule of water, yielding a *substance*, $C_{17}H_{13}ON_5$, which forms white needles, m. p. 242°.

Ost's nitrosodipyromeconic acid also yields a *quinoxaline*, $C_{11}H_7O_2N_3$, when treated with *o*-phenylenediamine hydrochloride in glacial acetic acid in the presence of sodium acetate. The substance forms lemon-

yellow crystals, gives a green coloration with sulphuric acid, and dissolves in alkali hydroxides, forming yellow solutions, from which the original substance is precipitated by carbon dioxide.

[With A. TAMBURELLO.]—In proof of the constitution previously given for Ost's pyromecazonic acid (2 : 3-dihydroxy-4-pyridone), it is found that the product of the reaction of its diacetyl derivative with diazomethane yields about the same figures for $-$OMe and $:$NMe groups when analysed by the methods of Zeisel and of Herzig and Meyer respectively. The pyromecazonic acid does not react with ethyl nitrate, and therefore does not contain a ketomethylenic grouping.

Ost's pyromecazone (obtained by oxidation of pyromecazonic acid) behaves in the same way when treated with diazomethane, for the yellow oil which is obtained contains only half the calculated amount of $-$OMe group. The action of diazoethane is different: the product, both from the free quinone and from its additive product with ethyl alcohol, contains almost the amount of $-$OEt group corresponding with the formula $C_5H_3O_2N{\cdot}OEt$. To the quinone the constitution

$$\begin{array}{l} \mathrm{CH{:}N{-\!\!-\!\!-}CO} \\ \mathrm{CH{\cdot}C(OH){\cdot}CO} \end{array}$$

is assigned. It gives the reddish-violet coloration with potassium hydroxide described by Bamberger as characteristic of *o*-quinones, and with *o*-phenylenediamine it forms a *quinoxaline*, $C_{11}H_7ON_3$, which crystallises in canary-yellow needles, and for which the formula $\begin{array}{l}\mathrm{CH{\cdot}NH{\cdot}C{:}N} \\ \mathrm{CH{-}CO{-}C{:}N}\end{array}\!\!>C_6H_4$ is suggested. The *acetyl* derivative of the quinoxaline, $C_{13}H_9O_2N_3$, forms greenish-yellow needles.

In support of the conclusion that Ost's oxypyromecazonic acid is 1 : 2 : 3-trihydroxy-4-pyridone, the author finds that when a saturated aqueous solution of the substance is treated with ferric chloride, a red *iron* salt is precipitated, having the composition $Fe(C_5H_4O_4N)_3,3H_2O$. The acid also forms a *triacetyl* derivative, $C_5H_2O_4NAc_3$, which crystallises in aggregates of minute needles, m. p. 123—124°, and a *tribenzoyl* derivative, $C_5H_2O_4NBz_3$, crystallising in colourless needles, m. p. 162—163°. The position of the third hydroxyl group (attached to nitrogen) follows from the fact that it is readily reduced by tin and hydrochloric acid or by hydriodic acid, and from the production of the iron salt above mentioned.

[With A. TAMBURELLO.]—By the action of hydroxylamine on the ethers of comenic acid, derivatives of 1-hydroxypyridone can be obtained. When ethylcomenic acid is treated with hydroxylamine, an acid, $C_8H_9O_5N$, is obtained, m. p. 174—175° (with evolution of carbon dioxide). The substance gives a red coloration with ferric chloride. Its *ethyl* ester, $OEt{\cdot}C_5H_2O(CO_2Et){:}N{\cdot}OH$, forms colourless needles, m. p. 156°. The *acetyl* derivative, $OEt{\cdot}C_5H_2O(CO_2Et){:}N{\cdot}OAc$, forms rosettes of colourless needles, m. p. 81—82°. The action of hydroxylamine on ethyl ethylcomenate yields the above ethyl ester of m. p. 156°. To the acid of m. p. 174—175° the structure of 1-*hydroxy*-2-*ethoxy*-4-*pyridone*-6-*carboxylic acid* is ascribed. When it is reduced with tin and hydrochloric acid, it yields a substance, $C_8H_9O_4N$, which crystallises with $1H_2O$ in rosettes of colourless needles, m. p. 224—225°,

but when dehydrated (at 150°) it melts at 235° (decomp.). It gives an orange-yellow coloration with ferric chloride, and to it is assigned the constitution of 3-*ethoxy*-4-*pyridone*-6-*carboxylic acid*. It is identical with the product of the action of ammonia on ethylcomenic acid, and is also obtained by reduction of the ethyl ester above mentioned (m. p. 156°), since the ester is saponified at the same time. 3-Ethoxy-4-pyridone-6-carboxylic acid is hydrolysed when boiled for two hours with hydriodic acid (D 1·74), yielding 3-*hydroxy*-4-*pyridone*-6-*carboxylic acid* (Ost's comenamic acid). When 1-hydroxy-3-ethoxy-4-pyridone-6-carboxylic acid is kept at 190° for some time, 1-*hydroxy*-3-*ethoxy*-4-*pyridone* is obtained; it crystallises in colourless needles, m. p. 156°, and gives a brownish-red coloration with ferric chloride.

[With E. CARAPELLE.]—The phenylhydrazones of pyromeconic acid and some of their derivatives have also been investigated. When a solution of phenyldiazonium acetate is treated with a solution of pyromeconic acid at 0°, the *monophenylhydrazone*, $C_{11}H_8O_3N_2$, is produced; it forms dark red or purple crystals, which decompose at 176°. When it is treated with two molecules of phenylhydrazine, it yields two *triphenylhydrazones*, $C_5H_2O(:N\cdot NHPh)_3$, which are apparently stereoisomeric. One of these has m. p. 161—162°, the other has m. p. 212—214°. The former is converted into the latter if hydrogen chloride is passed through its alcoholic solution for half an hour. The monohydrazone reacts with *o*-phenylenediamine, yielding a *quinoxaline*, $C_{17}H_{12}ON_4$. The monohydrazone is also readily converted into an hydroxypyridone derivative, and this indicates the analogy between its structure and that of oximinopyromeconic acid. When it is mixed with a little water and treated with sulphur dioxide at 0°, a substance, $C_{11}H_{10}O_3N_2$, is obtained, which forms crystalline scales, m. p. 220°, and is assigned the constitution of 1-*anilino*-2 : 3-*dihydroxy*-4-*pyridone*. Its *hydrochloride*, $C_{11}H_{10}O_3N_2,HCl$, crystallises in colourless needles. Its *diacetyl* derivative, $C_{11}H_8O_3N_2Ac_2$, crystallises in lustrous scales, m. p. 155—156°. 1-Anilino-2 : 3-dihydroxy-4-pyridone gives with ferric chloride a deep blue coloration, which disappears when excess of ferric chloride has been added. The *quinone* thus produced reacts with *o*-phenylenediamine, yielding a *quinoxaline*, $C_{17}H_{12}ON_4$, which forms golden-yellow scales, m. p. 181—182°. The quinone is best obtained by oxidising the pyridone with silver oxide, but it has been isolated only in the form of its *additive product* with methyl alcohol, $C_{11}H_8O_3N_2,MeOH$, which dissociates and melts (forming a red liquid) at 87—88°.

[With A. D'ANGELO.]—The authors have also prepared some derivatives of dibromocomenic acid. Dibromocomenic acid (compare Mennel, Abstr., 1883, 656) reacts with basic lead acetate, losing both atoms of bromine, and the corresponding *quinone* is formed, but could not be isolated. Both dibromocomenic acid and this quinone react with *o*-phenylenediamine, yielding a *quinoxaline*, to which the formula

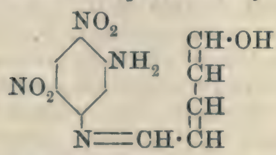
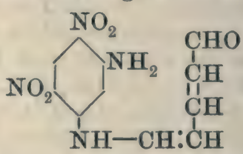
$$\begin{array}{l} CO_2H\cdot C{-}O{-}C:N \\ \quad\;\; \| \qquad\quad | \\ \quad\; CH\cdot CO\cdot C:N \end{array}\!\!>C_6H_4$$

is ascribed. It dissolves in alkalis, giving a yellowish-red coloration, and in concentrated sulphuric acid, giving a red coloration. When heated it decomposes above 200°. It yields a *phenylhydrazone*, which decomposes about 170°, to which the formula

$$\begin{array}{l} CO_2H\cdot C\text{—}O\text{————}C\colon N \\ \quad\;\; \| \qquad\qquad\qquad\quad | \\ \quad\; CH\cdot C(\colon N\cdot NHPh)\cdot C\colon N \end{array} \!\!>\! C_6H_4$$ is assigned. The phenylhydrazone yields the corresponding *xantho*-salt when treated with potassium hydroxide. The constitution of these substances is an argument in favour of the ketomethylenic formula for comenic acid. R. V. S.

4 : 6-Dinitrophenyl-1 : 3-dipyridinium Chloride and 4 : 6-Dinitro-3-aminopyridinium Chloride. THEODOR ZINCKE and G. WEISSPFENNING (*J. pr. Chem.*, 1912, [ii], 85, 207—210. Compare Abstr., 1910, i, 585).—When 4 : 6-dinitro-1 : 3-dipyridinium chloride is heated for five minutes with aniline in alcoholic solution, it is converted into 4 : 6-dinitro-3-aminophenylpyridinium chloride and the previously-described dianilide, $NPh\colon CH\cdot CH\colon CH\cdot CH\colon CH\cdot NHPh$, only one of the pyridine groups being removed. The further action of aniline on 4 : 6-dinitro-3-aminophenylpyridinium chloride results in the removal of the second pyridine group with the formation of the dianilide, together with 4 : 6-*dinitro*-m-*phenylenediamine*, which separates from glacial acetic acid in brownish-yellow crystals, m. p. 300°. If the action is continued for three to four hours, the dianilide disappears, and on the addition of hydrochloric acid, 4 : 6-dinitro-1 : 3-diaminobenzene hydrochloride and phenylpyridinium chloride (Abstr., 1904, i, 921) are obtained.

The successive action of excess of 2*N*-sodium hydroxide and hydrochloric acid on an aqueous solution of dinitroaminophenylpyridinium chloride yields a red, crystalline *substance*, $C_{11}H_{10}O_5N_4$, the constitution of which is represented by one of the following formulæ.

  .

This substance decomposes when heated, gives a reddish-violet coloration with alcoholic potassium hydroxide, and is reconverted by warm concentrated hydrochloric acid into dinitroaminophenylpyridinium chloride.

The interaction of dinitrophenyldipyridinium chloride and phenylhydrazine in alcoholic solution yields a deep black, crystalline *substance*, the composition of which is represented by one of the following formulæ :

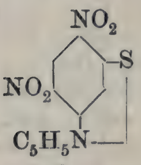
$$C_6H_2(NO_2)_2(N\colon CH\cdot CH\colon CH\cdot CH\colon CH\cdot NH\cdot NHPh)_2.$$
$$C_6H_2(NO_2)_2(NH\cdot CH\colon CH\cdot CH\colon CH\cdot CH\colon N\cdot NHPh)_2.$$

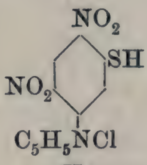
The same compound is produced by the action of phenylhydrazine on the blackish-green substance, $C_{16}H_{14}O_6N_4$, formed from dinitrophenyldipyridinium chloride and alkalis (Abstr., 1910, i, 585).

F. B.

Action of Hydrogen Sulphide on Dinitrophenylpyridinium and Dinitrophenyldipyridinium Chlorides. THEODOR ZINCKE and G. WEISSPFENNING (*J. pr. Chem.*, 1912, [ii], 85, 211—217).—The action of hydrogen sulphide on 4 : 6-dinitrophenyl-1 : 3-dipyri-

dinium chloride leads to the removal of one of the pyridine groups and the formation of a *thiobetaine anhydride* (I), similar in constitution to the anhydride previously described (Abstr., 1910, i, 585). The thiobetaine anhydride exists in two forms, an orange-red modification,


(I.)


(II.)

containing $1H_2O$, obtained by passing hydrogen sulphide into an aqueous solution of the pyridinium chloride, and a dark red form, which crystallises in leaflets and explodes on heating. The latter modification is produced by (1) the action of hydrogen sulphide on a 90% alcoholic solution of the pyridinium chloride, and (2) by dissolving the orange-red variety in concentrated hydrochloric acid and diluting the solution with water. The anhydride forms salts, which are instantly decomposed by water; the *hydrochloride* (II), prepared from the anhydride and hydrogen chloride in alcoholic solution, crystallises in white needles; the *platinichloride* is also described. The anhydride is converted by successive treatment with aqueous alkalis and acetic acid into an orange, crystalline *substance*, probably

$$SH\cdot C_6H_2(NO_2)_2\cdot N\colon CH\cdot CH\colon CH\cdot CH\colon CH\cdot OH.$$

A similar removal of the pyridine group takes place by the action of hydrogen sulphide on 2 : 4-dinitrophenylpyridinium chloride in aqueous solution, the product in this case consisting of 2 : 4-dinitrophenylmercaptan, accompanied by a small amount of 2 : 2′ : 4 : 4′(?)-tetranitrodiphenyl sulphide. The latter compound forms the main product when the hydrogen sulphide is replaced by sodium sulphide, or the action carried out in alcoholic solution. F. B.

Trinitrophenylpyridinium Chloride. THEODOR ZINCKE (*J. pr. Chem.*, 1912, [ii], **85**, 217—221. Compare Busch and Kögel, this vol., i, 50).—2 : 4 : 6-Trinitrophenylpyridinium chloride is best prepared by the interaction of picryl chloride and pyridine in ethereal solution. It has m. p. 128—129° (decomp.), and is resolved by alcoholic hydrogen chloride at 100° into its components; the yellow, crystalline *platinichloride*, $(C_{11}H_7O_6N_4Cl)_2PtCl_6$, has m. p. 255° (decomp.).

On successive treatment with hydrogen sulphide and hydrochloric acid, it yields a *substance*, which crystallises in dark violet leaflets of a metallic lustre. It reacts with aniline, forming the dianilide, $C_{17}H_{16}N_2$, previously described (Abstr., 1904, i, 921).

The *ψ-base*, $C_{11}H_8O_7N_4$, obtained by the action of alkalis, forms brown crystals, m. p. 190—193° (decomp.), yields a *sodium* salt, and is converted by acetic and hydrochloric acids into picramide and the original pyridinium salt. F. B.

Conversion of Oxindole into Coumaran-1-one. CHARLES MARSCHALK (*Ber.*, 1912, **85**, 582—585).—Oxindole has been transformed into coumaran-1-one by heating it with barium hydroxide in aqueous solution at 150°, converting the resulting barium *o*-aminophenylacetate (Baeyer and Comstock, Abstr., 1883, 1130) by means of

the diazo-reaction into *o*-hydroxyphenylacetic acid, and removing water from the latter compound by distillation. The diazotisation is accomplished by the addition of an aqueous solution of the barium salt and sodium nitrite to cold dilute sulphuric acid.

Oxindole is readily prepared by the reduction of isatin with sodium hyposulphite to dioxindole and subsequently reducing this by means of sodium amalgam in aqueous alcoholic solution. Dioxindole has m. p. 167—168°, and not 180° as given by Baeyer and Knop (*Annalen*, 1866, **140**, 11). When dissolved in aqueous sodium hydroxide and the solution treated with alcohol, it yields a crystalline *sodium* salt, which, however, is two unstable to be isolated, is converted by dilute sulphuric acid into dioxindole, but is apparently different from the sodium salt obtained by Baeyer and Knop by reducing isatin with sodium amalgam. F. B.

Some New Derivatives of Carbazole. BRUNO LEVY (*Monatsh.*, 1912, **33**, 177—184).—It has been discovered that the high temperature (170—190°) used by Graebe and von Adlerskron (Abstr., 1880, 660) in the preparation of methyl- and ethyl-carbazole was unnecessary, and that potassium carbazole reacts with methyl iodide almost quantitatively at the ordinary temperature. In extending the reaction to other alkyl halides, it is found that the velocity of the reaction decreases as the series is ascended, and also that the normal alkyl halides give a greater reaction velocity than the branched ones. Although no exact measurements were made, allyl iodide and benzyl chloride were found to react much more readily than ethyl iodide.

n-*Propylcarbazole* was obtained by the reaction of the iodide with potassium carbazole on the water-bath; it forms needle crystals, m. p. 50°, and gives a *picrate*, m. p. 98°.

iso*Propylcarbazole*, obtained similarly, has m. p. 120°, and gives a *picrate*, m. p. 143°.

n-*Butylcarbazole* forms needles, m. p. 58°, and gives a *picrate*, m. p. 89°. sec.-*Butylcarbazole* is an oil, which gives a *picrate*, m. p. 64°. iso*Butylcarbazole* is also an oil; the *picrate* has m. p. 177°.

iso*Amylcarbazole* is an oil; the *picrate* has m. p. 85°. sec.-*Amylcarbazole* is also an oil; m. p. of *picrate*, 93°.

Allylcarbazole, obtained by reaction at room temperature, crystallises in colourless rhombs, m. p. 56°; the *picrate* has m. p. 86°.

Benzylcarbazole, also prepared at the ordinary temperature, forms colourless needles, m. p. 114°; m. p. of *picrate*, 105°.

Triphenylmethylcarbazole, obtained by reaction of triphenylmethyl chloride and potassium carbazole in boiling benzene, forms rhombic crystals, m. p. 245°. D. F. T.

Thioamides. IV. Action of Hydrogen Sulphide on Nitrogen-substituted Aminoacetonitriles. TREAT B. JOHNSON and GERALD BURNHAM (*Amer. Chem. J.*, 1912, **47**, 232—242).—In an earlier paper (Abstr., 1911, i, 712) it has been shown that aminoacetonitrile reacts with hydrogen sulphide to form the corresponding thioamide, which is unstable and undergoes condensation in alcoholic

solution with production of thioglycylglycinethioamide. This thiopolypeptide is also unstable, and becomes converted into dithiopiperazine. The present investigation was undertaken in order to ascertain whether thioamides of *N*-substituted amino-acids of the type $R\cdot NH\cdot CH_2\cdot CS\cdot NH_2$ would undergo similar transformations. It has been found that phenylaminoacetonitrile, *p*-tolylaminoacetonitrile, anisoylaminoacetonitrile, hippuronitrile, carbethoxyaminoacetonitrile, and carbamidoacetonitrile all combine smoothly with hydrogen sulphide at the ordinary temperature to form the corresponding thioamides, which are stable compounds, and can be heated with alcohol without undergoing any change. When these thioamides are heated above their m. p.'s they suffer decomposition, but without producing a thiopolypeptide derivative or dithiopiperazine.

Hippurothioamide, $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot CS\cdot NH_2$, m. p. 150° (decomp.), crystallises in transparent blocks, and reacts with bromoacetophenone with production of 4-*phenyl*-2-*benzoylaminomethylthiazole*,

$$\begin{array}{l}CH{-}S\\ \,\|\\ CPh\cdot N\end{array}\!\!>C\cdot CH_2\cdot NHBz,$$

m. p. 148°, which forms rosettes of needles.

Carbethoxyaminoacetothioamide, $CO_2Et\cdot NH\cdot CH_2\cdot CS\cdot NH_2$, m. p. 118°, crystallises in rectangular blocks, and condenses with bromoacetophenone to form 4-*phenyl*-2-*carbethoxyaminomethylthiazole*,

$$\begin{array}{l}CH{-}S\\ \,\|\\ CPh\cdot N\end{array}\!\!>C\cdot CH_2\cdot NH\cdot CO_2Et,$$

m. p. 59—61°, which crystallises in prisms, and yields an unstable *hydrobromide*. When this hydrobromide is heated with hydrobromic acid, it is converted into 4-*phenyl*-2-*aminomethylthiazole hydrobromide*, $\begin{array}{l}CH{-}S\\ \,\|\\ CPh\cdot N\end{array}\!\!>C\cdot CH_2\cdot NH_2,2HBr$, m. p. 253° (decomp.).

Anisoylaminoacetonitrile, $OMe\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CN$, m. p. 153—154°, prepared by treating an aqueous solution of aminoacetonitrile sulphate with anisoyl chloride and potassium hydroxide, forms thin, transparent plates. *Anisoylaminoacetothioamide*,

$$OMe\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CS\cdot NH_2,$$

m. p. 189° (decomp.), crystallises in slender prisms.

Anilinoacetothioamide, $NHPh\cdot CH_2\cdot CS\cdot NH_2$, m. p. 166° (decomp.), forms stout blocks.

p-*Toluidinoacetothioamide*, $C_6H_4Me\cdot NH\cdot CH_2\cdot CS\cdot NH_2$, m. p. 152°, crystallises in rhombic plates or tabular prisms, and reacts with bromoacetophenone to form 4-*phenyl*-2-p-*toluidinomethylthiazole*, $\begin{array}{l}CH{-}S\\ \,\|\\ CPh\cdot N\end{array}\!\!>C\cdot CH_2\cdot NH\cdot C_6H_4Me$, m. p. 110—111°, which crystallises in prisms. When *p*-toluidinoacetonitrile is heated with phenylthiocarbimide, 2-*thio*-5-*phenylthiocarbamido*-1-*phenyl*-3-p-*tolyldihydroglyoxaline*, $NHPh\cdot CS\cdot NH\cdot C\!\!<\!\!\begin{array}{l}NPh\cdot CS\\ \quad\quad\; |\\ CH{-}N\cdot C_6H_4Me\end{array}$, m. p. 201°, is produced, which crystallises in bright yellow needles.

Carbamidoacetothioamide, $NH_2\cdot CO\cdot NH\cdot CH_2\cdot CS\cdot NH_2$, m. p. 190—191° (decomp.), forms colourless prisms, and condenses with bromoacetophenone with formation of 4-*phenyl*-2-*carbamidomethyl*-

thiazole, $\begin{matrix} CH—S \\ \| \\ CPh\cdot N \end{matrix}\!\!>\!C\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, m. p. 190°, which crystallises in slender needles, and yields a *hydrobromide*, m. p. 214° (decomp.).

E. G.

Formation of 1 : 3-Thiazines from Thiocarbamide. WILLIAM J. HALE and HARVEY C. BRILL (*J. Amer. Chem. Soc.*, 1912, 34, 295—300).—In an earlier paper (this vol., i, 216) it has been shown that carbamide condenses with nitromalonaldehyde with formation of 5-nitro-2-hydroxypyrimidine. It has now been found that the condensation of thiocarbamide with nitromalonaldehyde takes place in an entirely different manner.

When thiocarbamide and nitromalonaldehyde are allowed to react in aqueous solution in presence of a very small quantity of sodium hydroxide or diethylamine, the monothioureide of the aldehyde is produced. If piperidine is used as the condensing agent, however, 5-nitro-2-imino-1 : 3-thiazine separates, whilst a small amount of the thioureide remains in the mother liquor.

Nitromalonaldehyde monothioureide,

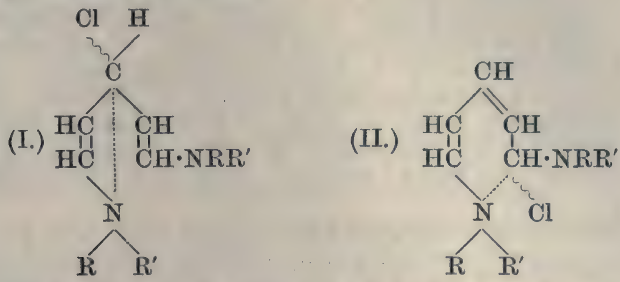
$$NH\!:\!C(SH)\cdot N\!:\!CH\cdot CH(NO_2)\cdot CHO,$$

m. p. 206—207° (corr.), crystallises in lustrous, yellow leaflets, and is readily desulphurised by treatment with basic lead acetate solution or mercuric oxide; its *potassium* salt forms reddish-brown crystals; the *lead* salt was also prepared. The *methyl ether*, m. p. 78—79° (corr.), obtained by the action of methyl sulphate on an aqueous solution of the potassium salt, forms yellow plates. Phenylhydrazine acetate reacts with the thioureide with formation of the *phenylhydrazone*. When the thioureide is suspended in alcohol and piperidine added, it is transformed into 5-nitro-2-imino-1 : 3-thiazine.

5-*Nitro-2-imino*-1 : 3-*thiazine*, $NO_2\cdot C\!\!<\!\!\begin{matrix} CH\cdot S \\ CH\!:\!N \end{matrix}\!\!>\!\!C\!:\!NH$, m. p. 151—152° (corr.), crystallises in long, yellow needles, and is not affected when boiled with an alkaline solution of lead acetate or with mercuric oxide. Phenylhydrazine and aniline do not have any effect on the compound, but benzenesulphonyl chloride reacts with it to form a yellow mass, thus establishing the presence of the imino-group. By the action of acetic anhydride, it is converted into the *acetyl* derivative, $NO_2\cdot C\!\!<\!\!\begin{matrix} CH\cdot S \\ CH\!:\!N \end{matrix}\!\!>\!\!C\!:\!NAc$, m. p. 141° (corr.). E. G.

A Peculiar Auxochrome Action. WALTER KÖNIG (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 221—223).—The colour of the pyridine dyes, obtained from pyridine and primary or secondary amines, is not satisfactorily accounted for by the usual formula: $NRR'\cdot CH\!:\!CH\cdot CH\!:\!CH\cdot CH\!:\!NClRR'$. The yellow colour of the simplest representative, obtained from methylaniline, becomes more green when the side-chain is lengthened by saturated alkyl groups, or when an ortho-substituent is introduced into the benzene ring. On the other hand, cyclic secondary amines, such as tetrahydroquinoline or dihydroindole, change the colour to red. These changes are

accounted for if one or other of the following formulæ is used, involving subsidiary valencies :



In accordance with Kaufmann's hypothesis, the subsidiary valency indicated by the dotted line should shift the colour more towards red the stronger it is. This is explained by a comparison with Kaufmann's views on benzene compounds. C. H. D.

Optically Active Hydrazino-acids. AUGUST DARAPSKY (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 215—216).—Hydrazino-acids of the formula $NH_2 \cdot NH \cdot CHR \cdot CO_2H$ have only been obtained in the racemic form by Traube (Abstr., 1896, i, 340) and Thiele (*ibid.*, 341) The author's simpler method of preparation (*Chem. Zeit.*, 1910, 34, 1280) allows of the preparation of the active modifications.

l-*Hydrazinophenylacetic acid*, $NH_2 \cdot NH \cdot CHPh \cdot CO_2H$, prepared from the *d*-chloro-acid and hydrazine hydrate, has $[\alpha]_D^{20} - 157 \cdot 8°$ in 2·7% solution in *N*/1-hydrochloric acid; the *d*-acid, prepared from the *l*-chloro-acid, has $[\alpha]_D^{20} + 158 \cdot 0°$. The rotation is nearly the same as that of the analogous amino-acid ($\pm 157 \cdot 9°$) and of the hydroxy-acid (mandelic acid, $\pm 157°$). *d*- and *l*-Hydrazinophenylacetic acids crystallise from water in silvery leaflets, m. p. 183—184° (racemic compound, 188—189°). Condensation with benzaldehyde yields active *benzylidene* compounds, crystallising from dilute alcohol in slender needles, m. p. 136—138°, whilst the racemic compound has m. p. 150°. The rotatory power is $[\alpha]_D^{20} \pm 166 \cdot 5°$ in acetone, 2·5% solution. It has not been found possible to resolve the racemic compounds. C. H. D.

Reduction of Aromatic Aldazines. THEODOR CURTIUS (*J. pr. Chem.*, 1912, 85, [ii], 137—188).—A continuation of previous work (this vol., i, 137).

[With FRITZ MAYER.]—2 : 4-*Dimethylbenzylhydrazine*,

$$C_6H_3Me_2 \cdot CH_2 \cdot NH \cdot NH_2,$$

is obtained as a colourless, viscid liquid, b. p. 136—137°/13 mm., by distilling the monohydrochloride (Abstr., 1900, i, 610) with calcium oxide under diminished pressure. It is very unstable, giving off nitrogen when kept, and is much less basic than the lower homologues previously described (Abstr., 1901, i, 573) ; its *dihydrochloride*, m. p. 164°, loses hydrogen chloride very readily, and is almost completely resolved into the monohydrochloride by crystallisation from alcohol. The *sulphate*, microscopic crystals, m. p. 163°, *oxalate*, m. p. 192°, and *picrate*, lustrous, yellow needles, m. p. 148°, are described.

On exposure to air, it is oxidised to 2 : 4-dimethylbenzaldehyde-2 : 4-dimethylbenzylhydrazone, m. p. 78° (Abstr., 1900, i, 610); the oxidation may also be effected by heating the hydrochloride with mercuric oxide and alcoholic sodium hydroxide. When heated with dilute hydrochloric acid, it yields 2 : 4-*dimethylbenzyl chloride*, $C_6H_3Me_2 \cdot CH_2Cl$, a colourless, viscid liquid, b. p. 103—104°/19 mm., having a pleasant aromatic odour. The *dibenzoyl* derivative, $C_6H_3Me_2 \cdot CH_2 \cdot N_2HBz_2$, crystallises in short, colourless columns, m. p. 169—170°; the *diacetyl* derivative, $C_{13}H_{18}O_2N_2$, forms colourless leaflets, m. p. 129°.

2 : 4-Dimethylbenzylhydrazine hydrochloride reacts with potassium cyanate in aqueous solution, yields 2 : 4-*dimethylbenzylsemicarbazide*, $C_6H_3Me_2 \cdot CH_2 \cdot N(NH_2) \cdot CO \cdot NH_2$, columnar crystals, m. p. 162°, and with phenylthiocarbimide and alcoholic potassium hydroxide, yielding *phenyl*-2 : 4-*dimethylbenzylthiosemicarbazide*,

$$C_6H_3Me_2 \cdot CH_2 \cdot N(NH_2) \cdot CS \cdot NHPh,$$

which crystallises in short, colourless columns, m. p. 138·5°.

a-2 : 4-*Dimethylbenzylhydrazonopropionic acid* is obtained as a yellow oil by the interaction of the hydrochloride, sodium acetate, and pyruvic acid in aqueous solution.

a-*Nitroso*-*a*-2 : 4-*dimethylbenzylhydrazine*, $C_6H_3Me_2 \cdot CH_2 \cdot N(NO) \cdot NH_2$, prepared from the hydrochloride and sodium nitrite, crystallises in colourless leaflets or needles, m. p. 60·5°; it reacts with 2 : 4-dimethylbenzaldehyde, yielding 2 : 4-dimethylbenzaldehyde-2 : 4-dimethylbenzylnitrosohydrazone (*loc. cit.*), and when heated at 80° with 10% sulphuric acid is converted into 2 : 4-*dimethylbenzylazoimide*, $C_6H_3Me_2 \cdot CH_2 \cdot N_3$. This forms a colourless liquid, b. p. 114°/15 mm., and is stable towards alkalis; it is hydrolysed by 20% sulphuric acid to hydrazoic acid and 2 : 4-dimethylbenzyl alcohol, small quantities of ammonia, 2 : 4-dimethylbenzaldehyde, 2 : 4-dimethylbenzylamine, and *m*-4-xylidine being produced simultaneously.

When heated with ethyl acetoacetate, 2 : 4-dimethylbenzylhydrazine yields *ethyl* β-2 : 4-*dimethylbenzylaminocrotonate*,

$$C_6H_3Me_2 \cdot CH_2 \cdot NH \cdot CMe{:}CH \cdot CO_2Et,$$

colourless leaflets, m. p. 85°, together with an oil, consisting probably of ethyl β-aminocrotonate. The formation of these two substances is considered to be due to the reduction of the hydrazine base by ethyl acetoacetate to ammonia and 2 : 4-dimethylbenzylamine, which then react with the ester to form ethyl β-aminocrotonate and ethyl β-2 : 4-dimethylbenzylaminocrotonate respectively.

3-*Phenyl*-1-op-*dimethylbenzyl*-5-*pyrazolone*,

$$\begin{matrix} CH_2 \cdot CO \\ | \\ CPh{=}N \end{matrix} \!\!> N \cdot CH_2 \cdot C_6H_3Me_2,$$

prepared by heating the hydrazine base with ethyl benzoylacetate, crystallises in colourless needles, m. p. 162°, dissolves in both acids and alkalis, and combines with *p*-toluenediazonium sulphate to form a scarlet-red *azo-dye*; its solution in aqueous ammonia gives sparingly soluble, crystalline precipitates with nickel, cobalt, copper, and silver salts.

4-*Oximino*-3-*phenyl*-1-op-*dimethylbenzyl*-5-*pyrazolone*, $C_{18}H_{17}O_2N_3$, obtained by the action of sodium nitrite on the preceding compound in

acetic acid solution, crystallises in slender, red needles, m. p. 128° (decomp.). On treatment with silver nitrate it forms a brownish-yellow *silver* salt, which becomes green when warmed with glacial acetic acid, and then has the composition $C_{18}H_{16}O_3N_3Ag$. The latter compound decomposes at 236°, and is probably the *silver* salt of 4-*nitro*-3-*phenyl*-1-op-*dimethylbenzyl*-5-*pyrazolone.*

3-*Phenyl*-1-op-*dimethylbenzyl*-2-*methyl*-5-*pyrazolone*, prepared from methyl iodide and the above-mentioned phenyldimethylbenzyl-pyrazolone, is a brown oil.

3-*Phenyl*-1-op-*dimethylbenzyl*-2-*methyl*-6-*pyridazinone*,

$$CH_2<\begin{matrix}CH_2\cdot CO\\CMe{=}N\end{matrix}>N\cdot CH_2\cdot C_6H_3Me_2,$$

is obtained by the interaction of dimethylbenzylhydrazine hydrochloride, sodium acetate, and lævulic acid in aqueous solution; it has m. p. 79·5°.

[With Hartwig Franzen.]—*aa*-*Di*-2 : 4 : 5-*trimethylbenzylhydrazine*, $NH_2\cdot N(CH_2\cdot C_6H_2Me_3)_2$, prepared from the hydrochloride (Abstr., 1901, i, 293) and sodium hydroxide in aqueous alcoholic solution, crystallises in white needles, m. p. 75°, and forms a *sulphate*, needles, m. p. 151°; *nitrate*, leaflets or needles, m. p. 118° (decomp.), and *platinichloride*, m. p. 95° (decomp.). It reacts with acetone, yielding *acetonedi*-2 : 4 : 5-*trimethylbenzylhydrazone*,

$$CMe_2{:}N\cdot N(CH_2\cdot C_6H_2Me_3)_2,$$

crystallising in small needles, m. p. 132°, and with *iso*butaldehyde to form iso*butaldehydedi*-2 : 4 : 5-*trimethylbenzylhydrazone*, $C_{24}H_{34}N_2$, m. p. 112°. When heated with acetic anhydride, it yields a *diacetyl* derivative, $C_{24}H_{32}O_2N_2$, m. p. 126°; the *monobenzoyl* derivative, $C_{27}H_{32}ON_2$, has m. p. 129°.

Di-2 : 4 : 5-*trimethylbenzylsemicarbazide*,

$$NH_2\cdot CO\cdot NH\cdot N(CH_2\cdot C_6H_2Me_2)_2,$$

prepared from the hydrochloride and potassium cyanate in aqueous solution, crystallises in needles or leaflets, m. p. 173°.

aa-Di-2 : 4 : 5-trimethylbenzylhydrazine forms an *ethiodide*,

$$C_{22}H_{33}N_2I,$$

white needles, m. p. 160°, and is oxidised by mercuric oxide in chloroform solution to *di*-2 : 4 : 5-*trimethylbenzyltetrazone*,

$$N(CH_2\cdot C_6H_2Me_3)_2\cdot N{:}N\cdot N(CH_2\cdot C_6H_2Me_3)_2,$$

which forms white needles or leaflets.

[With Reinhold Korte.]—p-Cuminaldazine, prepared from cuminaldehyde and hydrazine sulphate, has m. p. 111° (compare Gattermann, Abstr., 1906, i, 592). On reduction with sodium amalgam in alcoholic solution it yields p-*cuminaldehyde*-p-*cuminylhydrazone*, $C_6H_4Pr^{\beta}\cdot CH{:}N\cdot NH\cdot CH_2\cdot C_6H_4Pr^{\beta}$, which crystallises in small, lustrous, strongly refractive, yellowish-green columns of a rhombic habit, m. p. 75° (decomp.). The hydrazone is unstable, becoming oily when kept. It forms a *benzoyl* derivative, $C_{27}H_{30}ON_2$, m. p. 78°, and a *nitroso*-compound,

$$C_6H_4Pr^{\beta}\cdot CH{:}N(NO)\cdot CH_2\cdot C_6H_4Pr^{\beta},$$

crystallising in light yellow, felted needles, m. p. 59°. When heated in alcoholic solution, the nitroso-compound is converted into cuminaldazine.

s-*Di*-p-*cuminylhydrazine*, $N_2H_2(C_6H_4Pr^\beta)_2$, obtained by the prolonged reduction of cuminaldazine with sodium amalgam and alcohol, forms a white, wax-like mass, which rapidly decomposes; the *hydrochloride* crystallises in hexagonal plates, m. p. 217° (decomp.), the *diacetyl* derivative, $C_{24}H_{32}O_2N_2$, in large, rhombic columns, m. p. 71°. The *dinitroso*-derivative, $N_2(NO)_2(C_6H_4Pr^\beta)_2$, forms small tufts of yellow needles, m. p. 59°, and when heated in alcoholic solution yields the above-mentioned *p*-cuminaldehydenitroso-*p*-*iso*propylbenzylhydrazone, together with cuminaldazine and *di*-p-*cuminylidene*-*di*-p-*cuminyldihydrotetrazone*,

$$N_2(CH_2\cdot C_6H_4Pr^\beta)_2(N:CH\cdot C_6H_4Pr^\beta)_2,$$

m. p. 194°. The formation of the latter compound is considered to be due to the intermediate formation of *p*-cuminaldehyde-*p*-cuminylhydrazone, which is then oxidised by the nitrous acid, produced by the hydrolysis of the corresponding nitrosohydrazone, but all attempts to prepare the tetrazone by oxidising *p*-cuminylhydrazone with mercuric oxide in alcoholic or benzene solution proved unsuccessful, the sole product of the oxidation consisting of cuminaldazine.

p-*Cuminylhydrazine*, $C_6H_4Pr^\beta\cdot CH_2\cdot NH\cdot NH_2$, obtained in the form of its *hydrochloride* (slender needles, m. p. 199°, with previous sintering at 143°) by hydrolysing *p*-cuminaldehyde-*p*-cuminylhydrazone with dilute hydrochloric acid, has m. p. 46°; it is very unstable, and rapidly loses nitrogen at the ordinary temperature. The *nitroso*-compound, $C_6H_4Pr^\beta\cdot CH_2\cdot N(NO)\cdot NH_2$, forms very slender, felted needles, m. p. 63°, and when heated with 10% sulphuric acid is converted into p-*cuminylazoimide*, $C_6H_4Pr^\beta\cdot CH_2\cdot N_3$, a pale yellow oil, b. p. 118°/23 mm., which is stable towards alkalis, but is decomposed by 40% sulphuric acid with the evolution of nitrogen; hydrazoic acid is not produced.

[With Hermann Wewer].—*m*-Chlorobenzaldazine, m. p. 141° (compare Curtius and Melsbach, Abstr., 1910, i, 508), is reduced by zinc dust and glacial acetic acid in alcoholic solution to di-*m*-chlorobenzylamine. This crystallises from alcohol in small needles, m. p. 112°, and is identical with Berlin's "β-gechlortes Bibenzylamin" (*Annalen*, 1869, 151, 141). The following salts of the amine are described: the hydrochloride, m. p. 227°; nitrate, m. p. 203°; *platinichloride*, brown needles, m. p. 222° (decomp.), and *nitrite*, lustrous, white needles, m. p. 133°.

Di-m-*chlorobenzylnitrosoamine*, $NO\cdot N(CH_2\cdot C_6H_4Cl)_2$, prepared by boiling an alcoholic solution of the nitrite, forms clusters of yellowish-white needles, m. p. 53°, and is reduced by zinc and acetic acid in alcoholic solution to di-*m*-chlorobenzylamine and *aa*-*di*-m-*chlorobenzylhydrazine*, $NH_2\cdot N(CH_2\cdot C_6H_4Cl)_2$, which reacts with benzaldehyde, yielding *benzaldehyde*-*di*-m-*chlorobenzylhydrazone*,

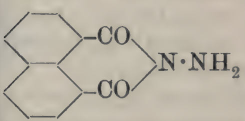
$$CHPh:N\cdot N(CH_2\cdot C_6H_4Cl)_2.$$

This crystallises in small, yellow needles, m. p. 66°, and is hydrolysed by hydrochloric acid to benzaldehyde and *aa*-*di*-m-*chlorobenzylhydrazine hydrochloride*, white leaflets, m. p. 200°. On treatment with sodium nitrite the preceding hydrochloride yields di-*m*-chlorobenzylamine nitrite.

s-*Di*-m-*chlorobenzylhydrazine*, $N_2H_2(CH_2\cdot C_6H_4Cl)_2$, prepared by reducing m-chlorobenzaldazine with sodium amalgam and alcohol,

crystallises in small, white needles, m. p. 43°; the *hydrochloride*, yellowish-white needles, m. p. 191°, the *dibenzoyl* derivative, m. p. 88°, and the *diacetyl* derivative, m. p. 73°, are described. The yellow *nitroso*-derivative, $N_2(NO)_2(CH_2{\cdot}C_6H_4Cl)_2$, m. p. 48°, when heated in alcoholic solution is converted into m-*chlorobenzaldehydenitroso*-m-*chlorobenzylhydrazone*, $C_6H_4Cl{\cdot}CH{:}N{\cdot}N(NO){\cdot}CH_2{\cdot}C_6H_4Cl$, which forms yellow needles, m. p. 98°, and is hydrolysed by hydrochloric acid to m-*chlorobenzylhydrazine hydrochloride*, $C_6H_4Cl{\cdot}NH{\cdot}NH_2,HCl$, colourless needles, m. p. 134°. F. B.

***N*-Aminonaphthalimide and its Derivatives.** ADRIANO OSTROGOVICH and M. MIHAILESCU (*Gazzetta*, 1911, 41, ii, 757—807). —By the action of hydrazine sulphate on naphthalic anhydride the authors have obtained *N*-aminonaphthalimide, for which the annexed symmetrical formula is to be adopted in view of the reactions of the substance described below. The same substance is obtained when naphthalimide, or even naphthalic acid, is taken instead of naphthalic anhydride.



N-*Aminonaphthalimide* is obtained by treating a boiling solution of naphthalic anhydride in glacial acetic acid with a boiling aqueous solution of hydrazine sulphate and sodium acetate. Ebullition is continued for a few minutes, and, on cooling, the imide, $C_{12}H_8O_2N_2$, is deposited in long, lemon-yellow needles, m. p. 262° after recrystallisation. The same substance is obtained by heating hydrazine sulphate and sodium acetate with a solution of naphthalimide in aqueous glacial acetic acid for some hours in a sealed tube at 200—220°. The imide can also be prepared by boiling hydrazine sulphate (or, better, hydrochloride) with a solution of naphthalic acid in aqueous potassium hydroxide. *N*-Aminonaphthalimide is a stable substance, which sublimes unchanged and is not attacked by boiling concentrated acids or alkalis. It dissolves in boiling concentrated alkalis, however, and is reprecipitated by carbon dioxide, but the solution is not to be ascribed to the production of a metallic derivative. The *sulphate* is obtained in tabular, colourless crystals by adding concentrated sulphuric acid to a solution of the base in glacial acetic acid; it is stable only in the presence of sulphuric acid of sufficient concentration. The *hydrochloride* forms small, colourless needles, and is immediately hydrolysed by traces of moisture. The *platinichloride*,

$$(C_{12}H_8O_2N_2)_2,H_2PtCl_6,$$

is an orange-yellow, crystalline powder. The *picrate*,

$$C_{12}H_8O_2N_2{\cdot}C_6H_3O_7N_3,$$

forms orange-yellow needles, m. p. 192°. When treated with sodium nitrite in the presence of glacial acetic acid, *N*-aminonaphthalimide yields naphthalimide, identical with that of Jaubert (Abstr., 1895, i, 239), and nitrous oxide is evolved. With sodium hypobromite, *N*-aminonaphthalimide yields naphthalimide according to the equation:

$$2C_{12}H_8O_2N_2 + NaOBr = NaBr + H_2O + N_2 + 2C_{12}H_7O_2N.$$

N-Aminonaphthalimide yields acyl derivatives, for the convenient naming of which the author proposes the term naphthalimyl to denote

the group $C_{10}H_6<\substack{CO\\CO}>N-$. For these derivatives the two tautomeric forms R·NH·CO·R′ and R·N:C(OH)·R′ are possible, but the enolic formula is excluded, because the substances give no coloration with ferric chloride. *Formyl*-N-*aminonaphthalimide*,

$$C_{12}H_6O_2:N \cdot NH \cdot CHO,$$

is obtained by heating *N*-aminonaphthalimide with formamide at 140° for about an hour; it forms almost colourless, prismatic crystals, m. p. 245—246°. It is a very stable substance, which dissolves unchanged in cold, strong acids or alkalis, and is hydrolysed only when these solutions are boiled. *Acetyl*-N-*aminonaphthalimide*, $C_{12}H_6O_2N_2H \cdot Ac$, obtained by boiling *N*-aminonaphthalimide with an excess of acetic anhydride, crystallises in colourless needles, m. p. 260—261°; in stability it resembles the formyl derivative. *Benzoyl*-N-*aminonaphthalimide*, $C_{12}H_6O_2N_2HBz$ (from benzoic anhydride), forms colourless needles, which begin to soften at 280° and melt at 290—291°, and is also very stable towards acids and alkalis.

N-Aminonaphthalimide reacts with the anhydrides of dibasic acids, giving, in the case of phthalic and naphthalic anhydrides, the corresponding imide, one molecule of water being eliminated; succinic, maleic, and citraconic anhydrides yield amic acids, from which the imides may be obtained by dehydration. N-*Naphthalimidosuccinamic acid* (termed N-*naphthalimylsuccinamic acid* by the author),

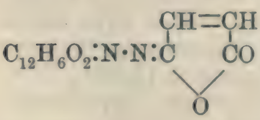
$$C_{12}H_6O_2:N \cdot NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H,$$

obtained by the interaction of *N*-aminonaphthalimide and succinic anhydride, either in the warm or at the ordinary temperature, forms acicular crystals, m. p. 213° (with evolution of gas, presumably steam). When it is boiled with glacial acetic acid or heated at 180° in a current of dry air, N-*naphthalimidosuccinimide*,

$$C_{12}H_6O_2:N \cdot N:C_4H_4O_2,$$

is produced; it is a white, crystalline powder, which begins to ball together towards 260°, and melts at 272—273°. This imide may be reconverted into the acid by dissolving it in dilute potassium hydroxide and adding a slight excess of dilute acetic acid or hydrochloric acid.

N-*Naphthalimidomaleinamic acid*, $C_{12}H_6O_2:N \cdot NH \cdot CO \cdot CH:CH \cdot CO_2H$, is a white, microcrystalline powder, m. p. 205° (decomp.). It is probably the *cis*-form, because it does not absorb bromine, and it does yield an imide. The *ammonium* salt and the *silver* salt, $C_{16}H_9O_5N_2Ag$, were prepared. N-*Naphthalimidomaleinimide*, $C_{12}H_6O_2:N \cdot N:C_4H_2O_2$, is obtained with some difficulty; it is necessary to boil the acid for some minutes with a large excess of acetyl chloride. It forms minute, acicular, colourless crystals, m. p. 118—120°; if the heating is continued, it resolidifies at 150° and melts again at 215°. The authors suppose that the treatment with acetyl chloride yields the unsymmetrical imide (annexed formula), which when heated above its melting point is transformed into the symmetrical imide; in one preparation this isomeride was obtained direct, crystallising in small, colourless needles, m. p. 240°. *N*-Naphthalimidomaleinimide gives Piutti's reaction (with sodium methoxide or ethoxide) for substituted unsaturated imides.



N-*Naphthalimidocitraconamic acid*, $C_{12}H_6O_2{:}N{\cdot}NH{\cdot}C_5H_5O_3$, forms colourless, prismatic crystals. Like the corresponding maleinamic acid, it dissolves in alkalis, and is reprecipitated by dilute hydrochloric acid or sulphuric acid, but not by acetic acid. The ammonium and silver salts were prepared. N-*Naphthalimidocitraconimide*,

$$C_{12}H_6O_2{:}N{\cdot}N{:}C_5H_4O_2,$$

is obtained by heating the acid for some time at 140°, or by boiling it with glacial acetic acid. On heating it begins to soften at 250°, and melts at 254—255°. The imide can also be obtained by boiling *N*-aminonaphthalimide with an excess of citraconic anhydride. It gives Piutti's reaction.

N-*Naphthalimidophthalimide*, $C_{12}H_6O_2{:}N{\cdot}N{:}C_8H_4O_2$, is obtained by the interaction of *N*-aminonaphthalimide and phthalic anhydride in presence of glacial acetic acid or chloroform in the cold. It crystallises in colourless scales, m. p. about 320°. It dissolves readily in alkali hydroxides, and is reprecipitated by carbon dioxide.

N-*Naphthalimidonaphthalimide*, $C_{12}H_6O_2{:}N{\cdot}N{:}C_{12}H_6O_2$, is prepared by heating together equimolecular quantities of N-aminonaphthalimide and naphthalic anhydride at 240—260°. After cooling, the reaction product is dissolved in concentrated sulphuric acid, and the solution poured into an excess of water. It is a white, crystalline powder, m. p. about 330°. It dissolves in alkali hydroxides, and is reprecipitated by carbon dioxide. Neither this nor the preceding imide is attacked by hydrochloric acid; concentrated sulphuric acid hydrolyses them in the warm, yielding N-aminonaphthalimide.

Aldehydes react with *N*-aminonaphthalimide, giving in general the Schiff's bases resulting from the elimination of the elements of water. In the case of the aromatic aldehydes containing a *p*-hydroxy-group (*p*-hydroxybenzaldehyde, protocatechualdehyde, and vanillin) an intermediate additive product is formed, which can then be dehydrated. When the *p*-hydroxy-group is substituted, however (as in anisaldehyde, veratraldehyde, and piperonaldehyde), the condensation product is obtained direct. It was not possible to isolate a formaldehyde derivative.

Ethylidene-N-*aminonaphthalimide*, $C_{12}H_6O_2{:}N{\cdot}N{:}CHMe$, is obtained on mixing acetaldehyde with *N*-aminonaphthalimide; it forms small, colourless needles, m. p. 172°, and is readily hydrolysed.

Benzylidene-N-*aminonaphthalimide*, $C_{12}H_6O_2{:}N{\cdot}N{:}CHPh$ (obtained in presence of acetic acid or on warming with an excess of benzaldehyde), crystallises in colourless needles, m. p. 206—207°.

Cinnamylidene-N-*aminonaphthalimide*, $C_{12}H_6O_2{:}N{\cdot}N{:}CH{\cdot}CH{:}CHPh$, prepared in the same manner as the preceding derivative, forms small, colourless needles, m. p. 195—196°.

o-*Hydroxybenzylidene*-N-*aminonaphthalimide*,

$$C_{12}H_6O_2{:}N{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH,$$

crystallises in thin, colourless needles, m. p. 230—231°.

When a mixture of *N*-aminonaphthalimide and *p*-hydroxybenzaldehyde is kept in the presence of glacial acetic acid, the *additive product*, $C_{12}H_8O_2N_2{\cdot}C_7H_6O_2$, is obtained in the form of thin, colourless needles. If it is boiled with glacial acetic acid, p-*hydroxybenzylidene*-N-*aminonaphthalimide*, $C_{12}H_6O_2{:}N{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH$, is obtained; it

crystallises in slightly yellow prisms, which begin to soften at 270°, and melt at 283—284° (decomp.).

p-*Methoxybenzylidene*-N-*aminonaphthalimide*, $C_{12}H_6O_2:N\cdot N:C_8H_8O$, crystallises in colourless needles, which begin to ball together at 210°, and melt at 216—217°.

When resorcilaldehyde reacts with *N*-aminonaphthalimide, a mixture of the *additive product* and the imide is formed, which, on boiling with glacial acetic acid, yields 2 : 4-*dihydroxybenzylidene*-N-*aminonaphthalimide*, $C_{12}H_6O_2:N\cdot N:CH\cdot C_6H_3(OH)_2$, which crystallises in slightly yellow prisms, which become red about 180°, and then almost black, and melt at 289—290° (with slow heating); when placed in a bath at 285°, the substance becomes reddish-purple, balls together, and melts at 288—289° (decomp.).

N-Aminonaphthalimide and protocatechualdehyde, in presence of glacial acetic acid, yield an *additive product*, $C_{12}H_6O_2:N\cdot N:C_7H_6O_3$, a slightly yellow, microcrystalline powder, which, on heating, becomes brown at 260° and black at 280°. When it is boiled with glacial acetic acid, 3 : 4-*dihydroxybenzylidene*-N-*aminonaphthalimide*, $C_{12}H_6O_2:N\cdot N:CH\cdot C_6H_3(OH)_2$, is obtained; it crystallises in small, pale yellow prisms.

N-Aminonaphthalimide and vanillin in presence of glacial acetic acid yield the *additive product*,

$$C_{12}H_6O_2:N\cdot NH\cdot CH(OH)\cdot C_6H_3(OH)\cdot OMe;$$

it crystallises in tufts of yellow needles, which soften and ball together about 220°, and melt at 226—227°. When it is heated at 130—140° (or at 160°), or boiled with glacial acetic acid, it yields 4-*hydroxy*-3-*methoxybenzylidene*-N-*aminonaphthalimide*,

$$C_{12}H_6O_2:N\cdot N:CH\cdot C_6H_3(OH)\cdot OMe,$$

which crystallises in long, colourless needles, softens about 228°, and melts at 231—232°.

3 : 4-*Dimethoxybenzylidene*-N-*aminonaphthalimide*,

$$C_{12}H_6O_2:N\cdot N:CH\cdot C_6H_3(OMe)_2,$$

is obtained by keeping an alcoholic solution of *N*-aminonaphthalimide and veratraldehyde for two days; it forms colourless needles, m. p. 229—230°.

Piperonylidene-N-*aminonaphthalimide*,

$$C_{12}H_6O_2:N\cdot N:CH\cdot C_6H_3:O_2:CH_2,$$

obtained from piperonaldehyde in glacial acetic acid at the ordinary temperature, forms small, colourless needles, m. p. 256—257°.

When *N*-aminonaphthalimide is boiled with an excess of *p*-benzoquinone in glacial acetic acid, N-*naphthalimido*-p-*benzoquinonemonoimine*, $C_{12}H_6O_2:N\cdot N:C_6H_4:O$, is obtained as a slightly brown, microcrystalline precipitate. The compound is soluble in alkali hydroxides, giving an orange or red coloration, and is reprecipitated by dilute hydrochloric acid or carbon dioxide. The substance dissolves in concentrated sulphuric acid, giving a red solution with a violet tinge, and is precipitated unaltered on addition of water. R. V. S.

Condensation of 5(4)-Methylglyoxaline with Chloral. OTTO GERNGROSS (*Ber.*, 1912, 45, 509—526. Compare Abstr., 1909, i, 189).—The condensation of 4-methylglyoxaline with chloral is

analogous to that with formaldehyde (Windaus, Abstr., 1909, i, 258), the chloral becoming attached to the ring in position 5 (or 4), namely, $CH{<}{\substack{NH\cdot CMe\\ N-C\cdot CH(OH)\cdot CCl_3}}$.

The ester hydrochloride, $HCl,CH{<}{\substack{NH\cdot CMe\\ N-C\cdot CHCl\cdot CO_2Me}}$, and the hydrochloride of the corresponding acid contain an extremely labile chlorine atom. In aqueous solution at 0° the chlorine is precipitated completely by silver nitrate; when the aqueous solution is evaporated the hydrochloride of the hydroxy-acid is formed quantitatively. This chlorine atom reacts with sodium methoxide with the formation of the methoxy-compound, $HCl,CH{<}{\substack{NH\cdot CMe\\ N-C\cdot CH(OMe)\cdot CO_2Me}}$.

When the hydroxy-acid is warmed with dilute nitric acid, a mixture of two nitrates is obtained, which are separated by boiling with 90% alcohol. The faintly basic nitrate of the α-ketonic acid is hydrolysed, whereas the more basic nitrate of 4-methylglyoxaline-5-carboxylic acid remains in solution.

The ketonic acid, $CH{<}{\substack{NH\cdot CMe\\ N-C\cdot CO\cdot CO_2H}}$, forms a crystalline oxime with a characteristic sodium salt. When heated with aniline, carbon dioxide is eliminated, and the base, $CH{<}{\substack{NH\cdot CMe\\ N-C\cdot CH:NPh}}$, formed. When reduced with aluminium amalgam the hydroxy-acid is reformed.

5(4)-Methylglyoxaline-4(5)-carboxylic acid, $CH{<}{\substack{NH\cdot CMe\\ N-C\cdot CO_2H}}$, is the main product of the oxidation of methylglyoxalineglycollic acid with concentrated nitric acid. The ethyl ester of this acid is obtained synthetically on boiling thioglyoxaline with 10% nitric acid.

The *hydrobromide* of 5(4)-*methylglyoxalineglycollic acid* crystallises in short, pointed needles, m. p. 184—185° (decomp.). The *hydrobromide* of the *ester* is obtained in lancet-shaped crystals pointed at both sides, which sinter at 160°, m. p. 166° (decomp.); the *hydrochloride* of the acid crystallises in four-sided prisms, m. p. 183—184° (decomp.); that of the *ester* forms rhombic and lancet-shaped platelets, which sinter at 147°, m. p. 150·5°.

5(4)-*Methylglyoxaline*-4(5)-*glycollic acid* crystallises in well-formed, lustrous plates and stunted prisms, which become brown at 205°, m. p. 215°, to a reddish-brown foam. The *nitrate* crystallises in long, six-sided plates, decomp. 150°; the *phosphotungstate* separates in microscopic needles; the *sodium* salt forms plates. The *copper* salt yields narrow, four-sided rods of a pale blue colour.

5(4)-*Methylglyoxaline*-4(5)-*chloroacetic acid hydrochloride*, prepared by the action of acetyl chloride on methyl methylglyoxalineglycollate hydrochloride, and isolated first in the form of the *methyl ester hydrochloride*, which crystallises in crossed needles sintering at 165°, m. p. 167° (decomp.), crystallises in stout, lustrous, four-sided, rhombic plates, which becomes yellow at 190°, m. p. 204° (decomp.).

5(4)-*Methylglyoxaline*-4(5)-*glyoxylic acid* crystallises in short rods and needles, which become brown at 230° and begin to decompose at 240°. The *sodium* salt forms transparent, four-sided plates with oblique ends; the *nitrate* has pointed crystals, which begin to decompose at 200°; the *hydrochloride* crystallises in six-sided plates, which become brown at 235° and decomp. at 242°. The *oxime* crystallises in needles, which sinter at 225°, m. p. 228° (decomp.); it forms a characteristic *sodium* salt, crystallising in thin, flat needles, m. p. 210° (decomp. to a black mass).

Methylglyoxalineglyoxylic acid, when reduced by aluminium amalgam in alcoholic aqueous sodium hydroxide solution, is converted into methylglyoxalineglycollic acid.

The *anil* of 5(4)-*methylglyoxaline*-4(5)-*aldehyde* crystallises in sharp needles, m. p. 224° (decomp. to blackish-brown drops).

5(4)-*Methylglyoxaline*-4(5)-*carboxylic acid*, prepared by oxidation of methylglyoxalineglycollic acid with concentrated nitric acid, crystallises in long, thin, matted needles, m. p. 223° (decomp.), and sublimes in flat needles when heated above 200°. At the melting point carbon dioxide is eliminated, and methylglyoxaline formed. The *ammonium* salt is not stable; the *potassium* salt has decomp. 238°. The *hydrochloride* crystallises in lustrous platelets, m. p. 230° (decomp.); the *phosphotungstate* is obtained in small, thin, four-sided plates. The *ethyl* ester, prepared by heating the potassium salt with ethyl alcohol and ethyliodide, crystallises in long rods with oblique ends, m. p. 205—206°, and is identical with the product obtained synthetically from ethyl 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylate,

$$SH\cdot C\begin{matrix}\nearrow NH\cdot CMe \\ \quad\;\; \| \\ \searrow N - C\cdot CO_2Et\end{matrix}.$$

The *sodium* salt crystallises in long, slender needles, m. p. 240°; the *nitrate* forms four-sided plates, m. p. 167° (decomp.); the *hydrochloride* has m. p. 183° (some decomp.). The ester is hydrolysed on prolonged boiling with concentrated hydrochloric acid to 5(4)-methylglyoxaline-4(5)-carboxylic acid. E. F. A.

Constitution of the Supposed Pyrazolinecarboxylic Acid. CARL BÜLOW (*Ber.*, 1912, **45**, 528—533. Compare Bülow, this vol., i, 134).—Polemical. A reply to Buchner (this vol., i, 213). Pyrazoline compounds which contain no carboxyl group distil without decomposition, whereas Buchner's compound very readily loses nitrogen when heated; it is not believed possible for the carboxyl group to make this difference. Buchner's pyrazolidine from ethyl phenylpyrazolinedicarboxylate boils without decomposition, whereas the known pyrazolidines are very unstable. These and other reasons are quoted against assigning a pyrazoline structure to Buchner's compound. E. F. A.

Hydantoins. X. Action of Potassium Thiocyanate on Pyrrolidonecarboxylic Acid. 2-Thiohydantoin-4-propionic Acid. TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1912, **47**, 242—251).—Johnson and Nicolet (this vol., i, 53) have

shown that by the action of potassium thiocyanate on either glycine or acetylglycine in presence of acetic anhydride, the same 2-thio-3-acetylhydantoin is produced, and Johnson (*J. Biol. Chem.*, 1912, **11**, 97) has found that, under similar conditions, alanine and acetylalanine both yield the same 2-thio-3-acetyl-4-methylhydantoin. A study has now been made of the behaviour of potassium thiocyanate towards pyrrolidonecarboxylic acid in presence of acetic anhydride, and it has been found that the corresponding cyclic thiohydantoin is produced.

The *thiohydantoin* of *pyrrolidonecarboxylic acid*,

$$CH_2<\begin{matrix}CH_2\cdot CH\cdot CO\\ CO-N-CS\end{matrix}>NH,$$

m. p. 206° (decomp.), forms long, prismatic crystals, and is hydrolysed by dilute hydrochloric acid with production of 2-*thiohydantoin*-4-*propionic acid* (*thiohydantoin* of *glutamic acid*),

$$\begin{matrix}NH\cdot CO\\ CS\cdot NH\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot CO_2H,$$

m. p. 122°, which crystallises in rhombic plates. The latter thiohydantoin is readily desulphurised by chloroacetic acid with formation of *hydantoin-4-propionic acid* (*hydantoin* of *glutamic acid*),

$$\begin{matrix}NH\cdot CO\\ CO\cdot NH\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot CO_2H,$$

m. p. 165°, which crystallises in hexagonal, tabular prisms; this compound is also produced, but in smaller yield, by the action of chloroacetic acid on pyrrolidonecarboxylic acid thiohydantoin.

Attempts were made to synthesise 2-thiohydantoin-4-propionic acid by the action of potassium thiocyanate on glutamic acid dissolved in water, alcohol, or acetic anhydride, but without success. E. G.

Theory of the Indigo Vat. ARTHUR BINZ and KURT SCHÄDEL (*Ber.*, 1912, **45**, 586—597. Compare Abstr., 1911, i, 497).—The authors summarise the results of previous work in support of the view that in the formation of the indigo-vat, the indigotin is not directly reduced to indigo-white, but first combines with one or two molecules of sodium hydroxide (or other alkali hydroxide) to form an additive compound (compare Abstr., 1906, i, 749), from which oxygen is then removed by the reducing agent (for example, zinc) employed in the preparation of the vat:

$$C_{16}H_{10}O_2N_2 + NaOH = C_{16}H_{10}O_2N_2,NaOH$$
$$C_{16}H_{10}O_2N_2,NaOH + Zn = C_{16}H_{11}O_2N_2Na + ZnO.$$

If this interpretation is correct, the velocity of vat formation should be increased by replacing the free indigotin by the above-mentioned additive compound, and this is found to be the case. Zinc, iron, and magnesium react much more rapidly on the additive compound with sodium hydroxide than on indigotin in the presence of the same amount of free alkali.

Bromoindigotin and dibromoindigotin react with sodium ethoxide in alcoholic solution, yielding the *compounds*, $C_{16}H_{19}O_2N_2Br,NaOH$ and $C_{16}H_8O_2N_2Br_2,NaOH$, which are decomposed by washing with alcohol more readily than the corresponding compound of indigotin. The

alkali derivatives of the tetrahalogenoindigotins, on the other hand, are very stable.

With respect to the fixation of indigotin in the fibre, the authors consider that the first stage consists in the chemical union of the fibre with the indigo-white, and that this union remains intact during the subsequent oxidation. It is very improbable that a colloidal complex with the fibre is first produced, since it is found that colloidal indigotin cannot be fixed on the fibre. F. B.

Bromo- and Methoxy-derivatives of Indigotin. PAUL FRIEDLÄNDER, S. BRUCKNER, and G. DEUTSCH (*Annalen*, 1912, **388**, 23—49).—Dibromo- and dimethoxy-indigotins containing the substituents in positions 4 : 4′, 5 : 5′, 7 : 7′, and 6 : 6′ have been synthesised from the corresponding *o*-nitrobenzaldehydes or anthranilic acids with the object of ascertaining the influence of the substituents on the colours of the dyes. The colours of the first three dyes, in solution or on the fibre, do not markedly differ from that of indigotin itself; 6 : 6′-dichloro-, 6 : 6′-dibromo-, and 6 : 6′-dimethoxy-indigotin, however, exhibit a very different, reddish-violet shade.

6-*Bromo*-2-*nitrotoluene*, m. p. 38°, obtained from 2-nitro-*o*-toluidine by the Gattermann method in the cold, is reduced by tin, stannous chloride, and hydrochloric acid to 6-*bromo*-o-*toluidine*, a yellow oil, the *acetyl* derivative, m. p. 163°, of which is oxidised to *bromoacetylanthranilic acid*, $NHAc\cdot C_6H_3Br\cdot CO_2H$, m. p. 224°, by potassium permanganate at 80° in the presence of magnesium sulphate. This acid is converted by boiling sulphuric acid (1 : 1) into *m*-bromoaniline (*acetyl* derivative, m. p. 84°), but when hydrolysed by 10% sodium hydroxide yields 6-*bromoanthranilic acid*, m. p. 136°. The latter is boiled with an excess of chloroacetic acid in aqueous sodium carbonate, and the resulting 3-*bromophenylglycine*-2-*carboxylic acid* is converted in the usual manner into 4 : 4′-*dibromoindigotin*, which crystallises from chloroform in blue needles with a copper lustre, exhibits pronounced dichroism in solution, and yields a normal vat with alkaline hyposulphite.

5 : 5′-Dibromoindigotin has already been prepared by Baeyer (*Ber.*, 1879, **12**, 1315). It is obtained by the direct bromination of indigotin in anhydrous solvents, and can also be produced from 5-bromoanthranilic acid. 4-*Bromophenylglycine*-2-*carboxylic acid* has m. p. 227—228° (decomp.).

6 : 6′-Dibromoindigotin, a constituent of the antique purple dye obtained from *Murex brandaris* (Abstr., 1909, ii, 262), has been prepared by Sachs from *p*-bromo-*o*-nitrobenzaldehyde (Abstr., 1904, i, 593). The authors prepare it in larger quantity from the bromoanthranilic acid (*acetyl* derivative, m. p. 217°). 5-*Bromophenylglycine*-2-*carboxylic acid*, m. p. about 236°, is a yellow, crystalline powder, and yields 6-*bromoacetylindoxyl*, m. p. 118·5°, by boiling with acetic anhydride and sodium acetate. Attempts to prepare 7 : 7′-dibromoindigotin from the bromoanthranilic acid have been unsuccessful. It has been obtained in very small yield by an application of Bauer's isatin synthesis (Abstr., 1907, i, 603). o-*Bromo-oxanilide*, m. p. 205°, is

boiled with phosphorus pentachloride in toluene, and the resulting *di-o-bromophenyloxaliminochloride*, $\begin{array}{l}CCl{:}N\cdot C_6H_4Br\\ |\\ CCl{:}N\cdot C_6H_4Br\end{array}$, m. p. 110°, yellow needles, is heated at 100° with 100% sulphuric acid, whereby 7-*bromoisatin*, $C_6H_3Br{<}{}^{NH}_{CO}{>}CO$, m. p. 192°, reddish-yellow needles, is obtained. 7-Bromoisatin responds to the indophenin test, and by warming in benzene with phosphorus pentachloride and subsequently treating the solution with hydrogen sulphide, yields 7 : 7′-*dibromoindigotin*, which crystallises in needles with a copper lustre.

Indoxyl condenses with 5 : 7-dibromoisatin chloride in benzene to form 5 : 7-*dibromoindigotin*, blue needles, and with 5 : 7-dibromoisatin in acetic acid to yield red needles of *dibromoindirubin*,

$$C_6H_2Br_2{<}\overset{NH\cdot CO}{\longrightarrow}{>}C{:}C{<}{}^{CO}_{NH}{>}C_6H_4.$$

2-*Amino*-6-*methoxybenzonitrile*, m. p. 141°, colourless needles, obtained by the reduction of 2-nitro-6-methoxybenzonitrile by tin, stannous chloride, and hydrochloric acid, forms an *acetyl* derivative, m. p. 176°, and is not hydrolysed by acids or alkalis, dilute or concentrated, hot or cold, but is slowly attacked by very concentrated sodium hydroxide at 160—170°, yielding 2-*amino*-6-*methoxybenzamide*, m. p. 150°. This substance, unlike the nitrile, reacts readily with chloroacetic acid in boiling, concentrated sodium carbonate, yielding 3-*methoxyphenylglycine*-2-*carboxylamide*, $NH_2\cdot CO\cdot C_6H_3(OMe)\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 208° (decomp.), yellow crystals, from which sodium hydroxide at 170—190° or boiling acetic anhydride and sodium acetate (and atmospheric oxygen) produce 4 : 4′-*dimethoxyindigotin*, needles with a copper lustre.

5 : 5′-*Dimethoxyindigotin*, blue needles with a copper lustre, is obtained from 2-nitro-5-methoxybenzaldehyde, acetone, and dilute sodium hydroxide in the usual manner.

2-Acetylamino-*p*-cresol and methyl sulphate in alkaline solution yield the *methyl ether*, $OMe\cdot C_6H_3Me\cdot NHAc$, m. p. 95° (the corresponding *ethyl ether* has m. p. 126°). These ethers are oxidised to the corresponding acids by boiling aqueous potassium permanganate and magnesium sulphate. 4-*Methoxyacetylanthranilic acid*, m. p. 199° (decomp.), and 4-*ethoxyacetylanthranilic acid*, m. p. 182—183°, yield by hydrolysis with dilute sulphuric acid (1 : 1) 4-*methoxyanthranilic acid*, m. p. 166° (decomp.) (*methyl* ester, m. p. 75°), and 4-*ethoxyanthranilic acid*, m. p. 174° respectively. These acids react with chloroacetic acid in boiling 10% sodium hydroxide, the products yielding, after acidification, 5-*methoxyphenylglycine*-2-*carboxylic acid*,

$$CO_2H\cdot C_6H_3(OMe)\cdot NH\cdot CH_2\cdot CO_2H,$$

m. p. 159—161° (decomp.), brown, microscopic needles, and 5-*ethoxyphenylglycine*-2-*carboxylic acid*, m. p. 166—167°, red, microscopic needles respectively, from which the 6 : 6′-*dialkyloxyindigotins* are obtained in the usual manner.

7 : 7′-*Dimethoxyindigotin*, needles with a copper lustre, is prepared from the nitromethoxybenzaldehyde, acetone, and sodium hydroxide.

C. S.

Action of Thioacetic Acid on Cyanoguanidine (Synthesis of Thioliminomethyltriazine). ADRIANO OSTROGOVICH (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 213—217. Compare Abstr., 1911, i, 1036).—When cyanoguanidine is heated with an ethereal solution of thioacetic acid for about two hours until the evolution of hydrogen sulphide ceases, 6-*thiol-2-imino-4-methyl*-1 : 3 : 5-*triazine*, $C_4H_6N_4S$, is precipitated. A further portion can be obtained from the solution, so that the total yield is 93%. The pure substance forms small, colourless crystals, which decompose without melting; for it the formula: $N{<}\begin{matrix}CMe{=\!=}N\\C(SH)\cdot NH\end{matrix}{>}C{:}NH$, or the tautomeric thionic form, is suggested. The compound is soluble in acids, in alkali hydroxides, and in ammonia.

R. V. S.

Researches on Purines. V. 2-Oxy-1-methylpurine. CARL O. JOHNS (*J. Biol. Chem.*, 1912, 11, 73—79).—Five of the six isomerides of 2-oxymethylpurine have been already described. The sixth, 2-oxy-1-methylpurine, can be obtained from 5 : 6-diamino-3-methyldihydro-2-pyrimidone. The potassium salt of nitrocytosine (5-nitro-6-aminodihydro-2-pyrimidone) is methylated by methyl iodide, and the product is found to be 5-*nitro*-6-*amino*-3-*methyldihydro*-2-*pyrimidone*, crystallising in slender prisms, m. p. 274° (decomp.). When this is reduced with freshly precipitated ferrous hydroxide, it gives a good yield of 5 : 6-*diamino*-3-*methyldihydro*-2-*pyrimidone*, which in turn reacts with formic acid to give a *formyl* derivative, the potassium salt of which when heated lost water and so formed the potassium salt of 2-*oxy*-1-*methylpurine*. This purine crystallises in flat prisms containing $2H_2O$; decomp. 280°. They effloresce in the air and become anhydrous over sulphuric acid. An aqueous solution gives sparingly soluble precipitates with platinum chloride and picric acid. The *picrate* has m. p. 214° (decomp.).

W. D. H.

A Purine–Hexose Compound. JOHN A. MANDEL and EDWARD K. DUNHAM (*J. Biol. Chem.*, 1912, 11, 85—86).—A preliminary note on a compound of adenine and hexose separated from an extract of yeast. It forms sheaves of delicate acicular crystals, and melts at 206°. Analysis shows close agreement with the figures calculated from the formula $C_{11}H_{15}O_5N_5$. A phenylosazone obtained from it yielded 15·3% nitrogen. The hexose has not yet been identified.

W. D. H.

Existence of Complexes between Purine Substances and Sodium Salicylate. GIOVANNI PELLINI and MARIO AMADORI (*Atti R. Accad. Lincei.*, 1912, [v], 21, i, 290—295. Compare Abstr., 1910, i, 525).—By measurements of the depression of the freezing point of aqueous solutions of sodium salicylate to which caffeine and theobromine, respectively, are added, the authors establish the existence of complexes similar to those formerly described. The tendency to their formation is more marked than in the case of sodium benzoate, and it is greater for caffeine than for theobromine.

Measurements of the solubility in water at 25° and at 40° of

pharmaceutical "sodium salicylate and caffeine" show that the product is not a mixture, as in the case of "sodium benzoate and caffeine," but on this point further experiments are needed. R. V. S.

Xanthine Derivatives from Uric Acid. IV. Preparation of Xanthine and Hypoxanthine. ERNST E. SUNDWIK (*Zeitsch. physiol. Chem.*, 1912, **76**, 486—488. Compare Abstr., 1911, i, 584).—Xanthine is formed to the extent of 30—33% when uric acid is heated at 200° with oxalic acid in presence of much glycerol.

Xanthine is converted into hypoxanthine by dissolving in excess of sodium hydroxide and shaking with chloroform at 60—70° during two hours. E. F. A.

Azoxy-compounds. ANGELO ANGELI and BRUNO VALORI (*Atti R. Accad. Lincei*, 1912, [v], **21**, i, 155—165. Compare Angeli and Alessandri, Abstr., 1911, i, 1045).—In the present paper two more pairs of isomeric azoxy-compounds are described, namely, *α*- and *β*-*p*-bromoazoxybenzene and *α*- and *β*-4-bromo-4′-nitroazoxybenzene.

When azoxybenzene is treated with bromine without a solvent, *α*-*p*-bromoazoxybenzene, $C_{12}H_9ON_2Br$, is obtained; it forms straw-yellow crystals, m. p. 73° (previously given as 75°). Oxidation of *p*-bromoazobenzene with hydrogen peroxide in glacial acetic acid solution, the mixture being kept at 40—50° for some days, yields *α*-*p*-bromoazoxybenzene, m. p. 73°, identical with that above described, and, in addition, *β-p-bromoazoxybenzene*, which forms yellow crystals, m. p. 92°. It is not possible to convert the two *p*-bromoazoxybenzenes into each other directly, and therefore they do not resemble the stereoisomeric azoxy-compounds of Reissert (Abstr., 1909, i, 435), but both the isomerides now described yield *p*-bromoazobenzene again on reduction with aluminium amalgam. *α*-*p*-Bromoazoxybenzene is not acted on by bromine, but *β*-*p*-bromoazoxybenzene when treated with bromine yields 4 : 4′-dibromoazoxybenzene. The constitutions of the two substances may be derived from this fact, because it is probable (in view of the formation of the bromo-derivatives about to be described, and of others already known) that a bromine atom attaches itself in the para-position in the nucleus in every NPh⁚ group. The authors therefore ascribe to *α*-*p*-bromoazoxybenzene the formula

$$Ph\cdot NO⁚N\cdot C_6H_4Br,$$

whilst *β*-*p*-bromoazoxybenzene is $NPh⁚NO\cdot C_6H_4Br$.

When bromine is added to *p*-nitroazobenzene in the presence of traces of iodine, 4-*bromo*-4′-*nitroazobenzene*, $C_{12}H_8O_2N_3Br$, is obtained; it forms dark red crystals, m. p. 203°. The bromination cannot be effected in glacial acetic acid even in sunlight. The action of nitric acid (D 1·45) on *p*-bromoazobenzene yields the same 4-bromo-4′-nitroazobenzene.

When *α*-*p*-bromoazoxybenzene is greatly warmed with nitric acid (D 1·45) a *compound*, $C_{12}H_8O_3N_3Br$, m. p. 99°, is obtained; in this substance the bromine and the nitro-group are probably attached to the same benzene nucleus. Treatment of *α*-*p*-bromoazoxybenzene with concentrated sulphuric acid for an hour on the water-bath leads to the production of *p*-bromoazobenzene and 4-bromo-4′-hydroxyazobenzene.

The addition of bromine to *p*-bromoazobenzene yields 4 : 4′-*dibromoazobenzene*, $C_{12}H_8N_2Br_2$, which forms dark orange-yellow cryst ls, m. p. 204°. If this substance is kept at 100° for twelve hours with hydrogen peroxide, 4 : 4′-dibromoazoxybenzene is obtained, identical with that prepared by brominating β-*p*-bromoazoxybenzene.

α-4-*Bromo*-4′-*nitroazoxybenzene*, $C_6H_4Br\cdot NO\colon N\cdot C_6H_4\cdot NO_2$, m. p. 194°, is obtained by keeping 4-bromo-4′-nitroazobenzene in glacial acetic acid solution with hydrogen peroxide at 100° for a day. β-4-*Bromo*-4′-*nitroazoxybenzene*, $C_6H_4Br\cdot N\colon NO\cdot C_6H_4\cdot NO_2$, is formed by treating β-*p*-nitroazoxybenzene, $NPh\colon NO\cdot C_6H_4\cdot NO_2$ (compare Angelo and Alessandri, *loc. cit.*), with bromine in the presence of iodine in the warm; it crystallises in minute, pale yellow prisms, m. p. 203°. Nitric acid (D 1·45) reacts with β-*p*-bromoazoxybenzene, yielding α-4-bromo-4′-nitroazoxybenzene, identical with that above described.

R. V. S.

Scission of Azo-dyes by Halogens. MAXIMILIAN P. SCHMIDT (*J. pr. Chem.*, 1912, [ii], **85**, 235—240).—*p*-Hydroxyazobenzene is converted by the action of chlorine or hypochlorous acid in aqueous solution into benzenediazonium chloride and 2 : 4 : 6-trichlorophenol, and by bromine into benzenediazonium bromide and 2 : 4 : 6-tribromophenol.

Sodium diazobenzenesulphonate when subjected to the same treatment also yields benzenediazonium salts (compare Fischer, Abstr., 1878, 302), and a similar decomposition has been observed in the case of a large number of azo-dyes.

With respect to the mechanism of the reaction, it is imagined that an additive compound with the halogen is first produced, which then undergoes decomposition as shown in the following scheme :

$$\begin{array}{c} R\cdot N \\ \| \\ OH\cdot R'\cdot N \end{array} \longrightarrow \begin{array}{c} R\cdot N\cdot Cl \\ | \\ OH\cdot R'\cdot N\cdot Cl \end{array} \longrightarrow \begin{array}{c} R\cdot N\cdot Cl \\ ||| \\ N \end{array} + HO\cdot R'\cdot Cl.$$

F. B.

Aromatic Substances Containing Multivalent Iodine. LUIGI MASCARELLI and B. TOSCHI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 145—151. Compare Mascarelli and Cerasoli, Abstr., 1910, i, 725; Mascarelli, Toschi, and Zambonini, *ibid.*, 831).—Attempts to prepare six-membered rings containing iodine have not been successful. Only in one case, namely, from the tetrazo-compound from 2 : 2′-diamino-4 : 4′-tetramethyldiaminodiphenylmethane, was a small quantity of a yellow powder obtained, which had m. p. 220—225°, and showed the properties of an *iodonium base*. In the present paper some *endo*-bisazo-derivatives (compare Duval, Abstr., 1910, i, 703, 781) are described, which were obtained during the course of the work.

When 2 : 2′-diamino-4 : 4′-dichlorodiphenylmethane is treated with nitrous acid, the tetrazo-compound is obtained. This reacts with potassium iodide, yielding 4 : 4′-dichloro-2 : 2′-di-iododiphenylmethane and a substance, $C_{13}H_6N_4Cl_2$, which crystallises in golden-yellow scales decomposing at 260—265°. To it is assigned the constitution

of pp′-*dichloro*endo*bisazodiphenylmethane*, $\underset{N_2\longrightarrow}{\overset{C_6H_3Cl}{|}}\!\!>C<\!\!\underset{N_2}{\overset{C_6H_3Cl}{|}}$. This compound when treated with sulphuric acid yields a crystalline substance (not analysed) which decomposes at 249—252°. Its alcoholic solution gives an intense green coloration with ferric chloride, and to it the constitution of 4 : 4′-*dichloro-2-hydroxy*endo*azodiphenylmethane* $OH\cdot C_6H_3Cl\cdot CH<\!\!\underset{N_2}{\overset{C_6H_3Cl}{|}}$, is ascribed.

4 : 4′-*Dichloro*-2 : 2′-*di-iododiphenylmethane tetrachloride*,

$$ICl_2\cdot C_6H_3Cl\cdot CH_2\cdot C_6H_3Cl\cdot ICl_2,$$

is obtained in yellow crystals, m. p. about 102° (evolving chlorine), when chlorine is passed through a chloroform solution of 4 : 4′-dichloro-2 : 2′-di-iododiphenylmethane. It is a very stable substance, and does not form iodoso- and iodoxy-derivatives when treated with the reagents which usually effect that change, and it was also impossible to obtain the di-iodoxy-derivative by oxidation with chlorine or with Caro's acid. R. V. S.

Azo -dyes from Substituted Pyrroles. HANS FISCHER and E. BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1912, **76**, 478—485).—In view of their importance for recognising and characterising blood and bile pigments, the azo-dyes from a number of substituted pyrroles have been prepared by interaction with diazobenzenesulphonic acid. Monoazo-compounds were obtained in all cases.

The *compound*, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_4NHMe_2\cdot COMe$, from 2 : 4-dimethyl-3-acetylpyrrole crystallises in long, lustrous, red needles.

The *compound*, $C_{15}H_{17}O_5N_3S$, from ethyl 2 : 5-dimethylpyrrole-3-carboxylate crystallises in long, greenish-olive, rhombic needles.

The *compound*, $C_{13}H_{13}O_5N_3S$, from 2 : 5-dimethylpyrrole-3-carboxylic acid separates in yellowish-brown needles.

The *compound*, $C_{12}H_{13}O_5N_3S$, from 2 : 5-dimethylpyrrole is obtained in tiny, microscopic, orange needles. The corresponding dye from 2 : 4-dimethylpyrrole crystallises in yellowish-brown needles.

Hæmopyrrole picrate has m. p. 125° (corr.); it does not readily condense with diazobenzenesulphonic acid. The free hæmopyrrole couples very readily, however, forming orange-yellow needles of the compound, $C_{14}H_{17}O_3N_3S$; it dissolves in concentrated sulphuric acid with a greenish-yellow coloration, and is totally different from the azo-dye obtained from 2 : 4-dimethyl-3-ethylpyrrole. E. F. A.

Losses in the Isolation of the Monoamino-acids [from Proteins] by the Ester Method. II. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, **77**, 59—74. Compare Abstr., 1911, i, 1049).—The pure amino-acids either singly or mixed were esterified, distilled, and hydrolysed, the amount recovered and the losses at each stage of the operation being determined. In this way the proportion recovered was from glycine 62·5%, from *d*-alanine 70%, and *dl*-leucine 80%. From a mixture of all five amino-acids there was obtained 50% of the glycine, 57% of the alanine, 66% of the leucine, 58% of the glutamic acid, and 40% of the *l*-aspartic acid. *d*-Valine is

recovered to the extent of 68%, *l*-phenylalanine only to the extent of 54%. In presence of protein the yields are still less.

It is considered that if these losses by the isolation of the monoamino-acids are taken into account, the proteins are almost entirely composed of the already known constituents. E. F. A.

Introduction of Iodine into Protein Derivatives. HERMANN PAULY (*Zeitsch. physiol. Chem.*, 1912, **76**, 291—292).—Basic nitrogenous substances exposed to the action of excess of iodine form brown periodides, in which the iodine is only loosely attached. Iodo-protein compounds must be colourless, and retain their iodine after treatment for a short time with sulphurous acid. The iodotryptophan described by Neuberg (Abstr., 1907, i, 955) is considered to be a periodide; it is not possible to introduce iodine into tryptophan or monobenzoyltryptophan. E. F. A.

Estimation of Amino-groups in the Oxyproteic Acids of Normal Urines. JÓZEF BROWINSKI and STEPHANE DĄBROWSKI (*Bull. Acad. Sci. Cracow*, 1911, *A*, 587—595; *Zeitsch. physiol. Chem.*, 1912, **77**, 92—106).—Determinations have been made of the ammonia and amino-nitrogen in the oxyproteic acids both before and after hydrolysis, using Sörensen's method of titration with formaldehyde.

Urochrome and *allo*oxyproteic acid before hydrolysis contain about 2·7% of ammonia nitrogen and 2·4%, and 6·4% respectively of amino-nitrogen. *anti*Oxyproteic and oxyproteic acids, which are not precipitated by basic lead acetate, contain no ammonia, but 11·2% and 38·8% respectively of amino-nitrogen. It is believed that the last two acids constitute the greater proportion of the oxyproteic acids of urine.

Hydrolysis with boiling hydrochloric acid leads to the formation of melanins and secondary products; hydrofluoric acid can be used to effect hydrolysis at the temperature of a boiling water-bath, and with it a much larger proportion of amino-acid nitrogen is obtained.

Melanin is formed from urochrome when hydrolysis with hydrofluoric acid is prolonged, but not from any other of the oxyproteic acids. This is taken to indicate that the oxyproteic acids are not to be regarded as the mother substances of the urinary pigment.

The proportions of ammonia and amino-nitrogen given by the four acids when decomposed with hydrofluoric acid for twenty-four hours are as follows: urochrome, NH_3 8·7%, NH_2 26·4%; *allo*oxyproteic acid, NH_3 4·2%, NH_2 76·9%, *anti*oxyproteic acid, NH_3 3·2%, NH_2 33·9%; oxyproteic acid, NH_3 8·3%, NH_2 80·5%. E. F. A.

Hæmoglobin. EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1912, **76**, 243—257. Compare Abstr., 1910, i, 599).—The absorption number (A) of hæmoglobin solutions, that is, the ratio of concentration (c) to the extinction coefficient (e), should be a constant independent of the apparatus used and the observer, if the method is to be used to measure the concentration of hæmoglobin solutions. Measurements made to test this indicate the value $2·081 \times 10^{-3}$ for A, in agreement with Hüfner's original determinations, but differing from the value

1.87×10^{-3} determined by Butterfield, and previously used by the writer (Abstr., 1910, i, 599), whose values must be corrected accordingly. The amount of carbon monoxide fixed per gram of hæmoglobin is 1·36 c.c., which is in excellent agreement with the value 1·34 determined by Hüfner and by Butterfield. E. F. A.

The Behaviour of Carbon Monoxide Blood to Certain Precipitating Agents. KURT GESTEWITZ (*Zeitsch. exp. Path. Ther.*, 1911, Reprint 15 pp.).—Vegetable agglutinins, such as ricin and phasin, precipitate from carbon monoxide blood, the carboxyhæmoglobin in the corpuscles; zinc and copper salts precipitate it free from the corpuscles. The copper precipitate (produced by adding 1% copper sulphate solution) in normal blood is brown in colour, in carbon monoxide blood red, which is quite characteristic to the eye; no spectroscopic investigation is necessary. The colour difference with zinc salts is not so striking. The zinc carboxyhæmoglobin can be readily dried, and then remains undecomposed for weeks. W. D. H.

The Cleavage of Nucleic Acid by Organ Enzymes. ALFRED SCHITTENHELM and KARL WIENER (*Zeitsch. physiol. Chem.*, 1912, **77**, 77—85).—The experiments confirm on the whole the results of Levene and Medigreceanu, and relate to the enzymes concerned in nucleic acid cleavage in various tissue extracts; the products of cleavage inhibit the activity of the enzymes concerned. W. D. H.

Yeast Nucleic Acids. V. Structure of Pyrimidine Nucleosides. PHŒBUS A. LEVENE and FREDERICK B. LA FORGE (*Ber.*, 1912, **45**, 608—620. Compare Levene and Jacobs, Abstr., 1911, i, 96, 510).—The pyrimidine complexes in nucleic acid are very resistant towards the hydrolytic action of dilute mineral acids. When distilled with hydrochloric acid (D 1·06) for thirty-six hours, furfuraldehyde is liberated slowly, corresponding in amount with equimolecular proportions of ribose and base in the complex. When hydrolysed by hydrobromic acid in presence of bromine, cytidine is converted into 5-bromouracil and *d*-ribonic acid. Uridine or cytidine when treated with bromine in aqueous solution yields a solution which reduces Fehling's solution and forms a crystalline precipitate when heated with phenylhydrazine; this behaviour indicates that the double bond has remained intact.

When uridine is evaporated with concentrated nitric acid, an anhydride of two molecules of nitrouridinecarboxylic acid is obtained, which is readily converted into its ethyl or butyl esters, and when hydrolysed gives nitrouracil.

Alkyl derivatives of uridine or cytidine could not be obtained.

Both compounds are fairly easily reduced to dihydro-compounds, which are very easily hydrolysed by mineral acids, giving ribose and dihydro-derivatives of the bases. It is assumed that the glucoside formation between ribose and the base involves position 5 in the base, and that the contiguity of this to the double bond conditions the resistance to hydrolysis.

The preparation of uridine has been simplified by conversion of the

ribose into glucoside, which prevents its precipitation together with the base with lead acetate or barium hydroxide.

Cytidine is conveniently isolated as the sparingly soluble nitrate, m. p. 197°. The *free base* crystallises in long needles, which sinter at 220°, m. p. 230° (decomp.), $[\alpha]_D^{21}+29.63°$.

5-*Bromouridine* is very similar to uridine; it has m. p. 181—184°, $[\alpha]_D^{21}-15.4°$.

Hydroxyuridine (corresponding with 5-bromo-4-hydroxydihydrouracil) has m. p. 222—223°; the phenylhydrazide forms long, citron-yellow needles, m. p. 209°.

The *anhydride* of *nitrouridinecarboxylic acid*, $C_{18}H_{16}O_{17}N_6$, crystallises in short, thick prisms, decomp. above 200°; the *silver* salt is amorphous. The *ethyl* ester forms slender needles, decomp. above 200°; the n-*butyl* ester sinters at 185°, m. p. 190—192°.

Dihydrouridine is a colourless syrup, $[\alpha]_D+39.1°$. E. F. A.

Free Amino-groups of the Simplest Proteins. ALBRECHT KOSSEL and ALEXANDER T. CAMERON (*Zeitsch. physiol. Chem.*, 1912, 76, 457—463. Compare Kossel and Kennaway, Abstr., 1911, i, 667).—Nitroclupeine, obtained by nitration of clupeine, yields a nitroarginine on hydrolysis. This nitroarginine when treated with nitrous acid by van Slyke's process yields nitrogen corresponding with the decomposition of one amino-group. Since the amino-groups of guanidine and nitroguanidine are not decomposed by this reagent, the reactive amino-group can only be that of the ornithine residue, and the arginine groups of clupeine are linked in the following manner:

$$\cdots CO{\cdot}\underset{\displaystyle C_3H_6{\cdot}NH{\cdot}C(NH){\cdot}NH_2}{\underset{|}{NH}}\text{——}CO\text{——}NH\text{——}\underset{\displaystyle C_3H_6{\cdot}NH{\cdot}C(NH){\cdot}NH_2}{\underset{|}{CH}}\text{——}CO\text{——}NH\cdots$$

In further support of this formula it is shown that clupeine behaves similarly to guanidine when nitrated, it has the same acid-fixing power as the guanidine-groups in the molecule, and, lastly, unchanged clupeine gives no nitrogen by van Slyke's process.

Cyprinine, the protamine of carp sperm, contains at least 30·3% of its total nitrogen in the form of lysine; 23·6% of the total nitrogen is set free by nitrous acid.

In sturine about 6·9% of the total nitrogen is liberated; this roughly corresponds to the total amount of lysine present, but this quantity is not enough to make up all the acid-fixing groups of sturin.

E. F. A.

Electrical Transport of Colloids. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Zeitsch. physiol. Chem.*, 1912, 76, 385—387. Compare Pekelharing and Ringer, Abstr., 1911, i, 1051).—A criticism of the arrangement adopted by Pekelharing and Ringer in measuring the electrical transport of pepsin. It is regarded as important that the middle and side vessels should have exactly the same hydrogen ion concentration. E. F. A.

Compounds of Amino-acids and Ammonia. VII. PETER BERGELL and PAUL BOLL (*Zeitsch. physiol. Chem.*, 1912, 76, 464—467). —To establish whether the asymmetric hydrolysis of leucinamide was

brought about by a special enzyme or by the usual protein- or peptide-splitting enzymes, the effect of the addition of *N*-hydrochloric acid to the enzyme solution has been studied. The enzyme hydrolysing silk peptone was but little affected, those digesting casein and fibrin were only partly destroyed, but that acting on leucinamide was entirely killed, unchanged optically inactive leucinamide being recovered. Accordingly, the last change is attributed to a specific enzyme.

E. F. A.

Comparative Hydrolysis of Sucrose by Various Acids in Presence of Invertase. GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Bull. Soc. chim.*, 1912, [iv], 11, 176—186. Compare Abstr., 1898, ii, 128; 1909, i, 272; Sörensen, Abstr., 1910, i, 147; Euler and Ugglas, Abstr., 1910, i, 345, 796; Michaelis and Davidsohn, Abstr., 1911, i, 1051, 1052).—Previous investigations beginning with those of Kjeldahl in 1881 have shown that the activity of invertase and other enzymes is modified by the presence of acids or alkalis, but the conclusions arrived at as to the quantities of acids or alkalis that are most effective and as to the general laws governing these actions have been very variable.

In the present investigation account has been taken of the alkalinity of the yeast extract and of the sucrose solutions employed and disturbing influences due to these causes, and to variation in the yeast and the sucrose employed have been avoided. The results are summarised and tabulated in the original. They show that the acids, grouped according to their basicity, arrange themselves for activity at optimum concentrations, taking hydrochloric acid as 100, in the same order as for their catalytic activity on sucrose. Among the monobasic acids, trichloroacetic, dichloroacetic, and lactic acids are exceptional in their behaviour. The monobasic acids become more active as catalysts in presence of invertase, and this is also true, but to a less extent, for dibasic acids, whilst for tribasic acid the inverse holds. No explanation can be given at present of the exceptional behaviour of the three acids referred to already, or of the great increase in catalytic activity shown by aromatic sulphonic acids in presence of invertase.

T. A. H.

Cellulase. HANS VON EULER (*Zeitsch. angew. Chem.*, 1912, 25, 250—251).—A brief account of the work of earlier investigators on the action of bacteria and fungi on cellulose is given, and the conclusion is drawn that the hydrolysis of pure cellulose by enzymes derived from fungi or higher forms of plant life has not yet been demonstrated.

It is shown in the present communication that cellulose-dextrins, obtained by the action of strong sulphuric acid on cellulose, are converted under the influence of an enzyme (*cellulose-dextrinase*) occurring in the extract obtained by pressing *Merulius lacrimans* into substances having a greater reducing action on Fehling solution; that the change is brought about by an enzyme is demonstrated by the fact that very little change takes place if the extract is heated before being added to the cellulose-dextrin solution. W. H. G.

Synthetic Action of Enzymes. WILLIAM M. BAYLISS (*Proc. physiol. Soc.*, 1911–12, xl–xli; *J. Physiol.*, 43).—Using glycerol to reduce the water content, the synthesis by emulsin of quinol and dextrose to form arbutin can readily be observed in a week or less. A small degree of synthesis can readily be detected polarimetrically. This experiment lends itself well to class work. W. D. H.

The Nature of Enzyme Action. II. The Synthetic Properties of Anti-Emulsin. WILLIAM M. BAYLISS (*J. Physiol.*, 1912, 43, 455—466).—Intraperitoneal injection of emulsin does not give rise to any true anti-enzyme, although precipitins for the proteins contained in the solution are produced. The inhibitory action of serum so obtained on emulsin is no greater than that of normal serum, and is merely due to diminution of optimal acidity. Neither normal serum nor the immune serum has any synthetic action. Emulsin, on the other hand, will synthesise lactose and also the glucoside of glycerol. This synthesis is retarded by serum, probably owing to diminution of acidity. Emulsin is not a protein. W. D. H.

Influence of Protoplasmic Poisons on Reductase. D. FRASER HARRIS (*Bio-Chem. J.*, 1912, 6, 200—202).—The activity of this intracellular enzyme is not affected by reagents, such as chloroform, sodium fluoride, etc., which lessen the activity of, or destroy, protoplasm. W. D. H.

The Nitration of Arsanilic Acid. LUDWIG BENDA (*Ber.*, 1912, 45, 53—58).—The brownish-yellow substance obtained in addition to diazoarsanilic acid, mononitroarsanilic acid, and *s*-trinitroaniline in the nitration of arsanilic acid has the composition $C_6H_6O_7N_3As$.

As the action of bromine in alkaline solution gives 4-bromo-2:6-dinitroaniline (m. p. 158°, compare Austen, this Journ., 1876, ii, 513), and the action of potassium hydroxide yields 3:5-dinitro-4-hydroxyphenylarsinic acid (Benda and Bertheim, this vol., i, 63), the compound must be 3:5-*dinitro-4-aminophenylarsinic acid*. In the fact that it resists diazotisation, it resembles *s*-trinitroaniline. D. F. T.

Preparation of Aromatic Stibines. LUDWIG KAUFMANN (D.R.-P. 240316).—Triphenylstibine can be obtained in 80—90% yield and m. p. 53° (Michaelis and Reese give m. p. 48°) by boiling triphenylstibine sulphide (100 parts) with absolute alcohol (450 parts) and benzene (50 parts) during half an hour, adding copper powder, and continuing the heating during three hours; on cooling, the product separates in a pure condition. The copper can be replaced by iron in the presence of ferric chloride, or the mixture left at the ordinary temperature during about fifteen hours, and finally boiled for one hour. F. M. G. M.

Organic Chemistry.

Asphalt Theory of Naphtha-formation: New Work on the Genesis of Naphtha. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 354—359. Compare Abstr., 1904, ii, 180; 1905, ii, 43; 1907, i, 269; ii, 361; 1909, i, 39).—The naphtha synthesised by the method of Sabatier and Senderens (Abstr., 1907 i, 269) consists of unsaturated liquid hydrocarbons which have a high iodine number, and readily oxidise and become tarry. If, however, the catalytic substance is insufficiently heated, instead of a liquid product, a black, polymerised tarry substance resembling natural asphalt is obtained. The qualitative and quantitative resemblance between some of the fractions obtained on distilling naphtha and natural asphalt has already been pointed out by the author, and a similar resemblance is now found with the distillation products of this artificial asphalt.

The conclusion is drawn that the formation of naphtha is a more complex process than is assumed by the theories of Mendeléeff, Berthelot, and Cloëz, these only dealing with the initial stage of the process, namely, the formation of unsaturated hydrocarbons from carbides. These hydrocarbons, by a process of polymerisation, give solid natural bitumen (asphalt), which, on decomposition by heat or on spontaneous decomposition occupying countless years, yield liquid naphtha. This process is probably reversible, since naphtha, by oxidation or other processes, may be converted into more complex products similar to asphalt, and undoubtedly possessing a cyclic structure. Destructive distillation of the tarry matter formed by the condensation of naphtha gives a naphtha rich in paraffins. The author regards the asphalt theory of the formation of naphtha as definitely established.

T. H. P.

Preparation of Hydrocarbons with Two Double and One Triple Linking. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 241424).—*βε-Dimethylhexa-Δ^{αε}-dien-Δ^γ-inene*,

$$CH_2\!:\!CMe\cdot C\!:\!C\cdot CMe\!:\!CH_2,$$

a colourless oil, b. p. 32°/17 mm., was obtained by distilling the tetramethylglycol, $OH\cdot CMe_2\cdot C\!:\!C\cdot CMe_2\cdot OH$ (142 parts), with potassium hydrogen sulphate (50 parts) at 140—150° under atmospheric pressure, whilst *γη-dimethyl-Δ^δ-octinen-γη-diol*, $OH\cdot CMeEt\cdot C\!:\!C\cdot CMeEt\cdot OH$, colourless crystals, m. p. 53°, b. p. 126°/20 mm., when distilled with anhydrous oxalic acid furnished *γη-dimethylocta-Δ^{βη}-dien-Δ^δ-inene*, $CHMe\!:\!CMe\cdot C\!:\!C\cdot CMe\!:\!CHMe$, an oil, b. p. 71°/20·5 mm.

F. M. G. M.

The Inflammable Capacity of Mixtures of Methyl Chloride and Air. SAPOSHNIKOFF (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1911, **6**, 384).—A study of the combustion of mixtures of methyl chloride and air in varying proportions and at different temperatures. The heat of combustion of one kilo. of methyl chloride is 3099 calories, whereas

the corresponding figure for methane is 13,000; the conditions under which methyl chloride explodes are also considered in the original.

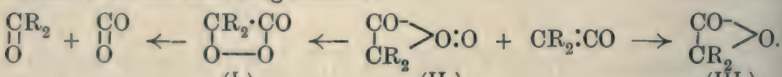
F. M. G. M.

Thermal Analysis of Hexachloroethane and of its Binary Mixtures. PAUL PASCAL (*Compt. rend.*, 1912, 154, 883—886).—The ordinary cooling curve for hexachloroethane reveals the existence of three modifications, the α-variety stable above 125°, the β-variety existing between 71·6° and 125°, and the γ-form, stable below 71·6°. The transition point 125° being ill defined on the curve, the accurate value was found from the curves for mixtures of the hexachloride with naphthalene and phenanthrene. Mixtures containing not more than 8% of naphthalene or 13% of phenanthrene show the unusual property of remaining solid at 71·6°, but undergoing partial liquefaction when the temperature falls slightly. The curves are reproduced and fully discussed in the original.

The cryoscopic constant for hexachloroethane is 560. W. O. W.

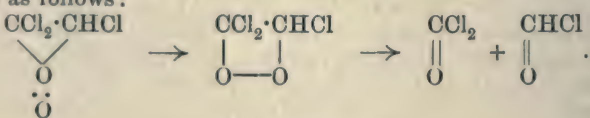
Autoxidation of Trichloroethylene. HERMANN STAUDINGER (*J. pr. Chem.*, 1912, [ii], 85, 330—333).—Remarks on Erdmann's paper on this subject (this vol., i, 65). From investigations on the autoxidation of the ketens, the author has come to the conclusion that the addition of oxygen to an autoxidisable substance, A, takes place unsymmetrically, thus: $A + >O{:}O \longrightarrow A{:}O{:}O$, and not symmetrically, $A<\begin{smallmatrix}O\\|\\O\end{smallmatrix}$, as hitherto imagined.

The autoxidation products of ketens consist of oxides of the type (I), which, in some cases, may be isolated, but readily decompose into ketones and carbon dioxide, together with oxides of the type (III), produced by the decomposition of the initial product (II), as shown in the following scheme:



(I.) (II.) (III.)

The author agrees on the whole with the views expressed by Erdmann on the autoxidation of trichloroethylene, but represents the formation of carbon monoxide, carbonyl chloride, and hydrogen chloride as follows:



F. B.

Ethylenic Isomerism of Acetylene Dichloride. GEORGES CHAVANNE (*Compt. rend.*, 1912, 154, 776—777).—Commercial acetylene dichloride consists of a mixture of two isomerides which can be separated by fractional distillation. The two compounds have b. p. 49°/760 mm. and 60·2°/760 mm. respectively. Both unite with bromine, yielding the same dibromide, m. p. −26°, b. p. 195°/760 mm.

W. O. W.

Action of Potassium Hydroxide on Tertiary Alcohols: New Method for the Diagnosis of Alcohols. MARCEL GUERBET (*Compt. rend.*, 1912, **154**, 713—715. Compare this vol., i, 67, 154).—Tertiary alcohols are scarcely attacked by potassium hydroxide below 230°. Above this temperature, oxidation slowly occurs, and the acids produced contain fewer carbon atoms than the original alcohol. Formic and propionic acids were recognised amongst the products from dimethylethylcarbinol, whilst a small amount of butyric acid was obtained from β-methylpentan-β-ol. W. O. W.

Catalytic Dehydration of Aliphatic Alcohols in the Wet Way by Sulphuric Acid. JEAN B. SENDERENS (*Compt. rend.*, 1912, **154**, 777—779. Compare Abstr., 1910, i, 649; 1911, i, 600—637).—Tertiary alcohols, even the lowest in the series, readily yield the corresponding ethylenic hydrocarbons when boiled with 3 to 4% of their volume of sulphuric acid. In the case of the secondary alcohols, this decomposition does not occur below the C_5 term, whilst with primary alcohols dehydration is inappreciable below the C_8 term. The function of the sulphuric acid appears to be purely catalytic, and not to depend merely on its capacity to absorb water. Its efficiency as a catalyst depends on the boiling point of the mixture, the low boiling alcohols only undergoing decomposition in presence of a relatively large amount of acid, whilst the high boiling, tertiary alcohols lose water equally readily in the presence of a much smaller proportion of acid. W. O. W.

Δ^{α}-Penten-δ-ol, $CH_2{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}OH$. HENRI PARISELLE (*Compt. rend.*, 1912, **154**, 710—712).—Magnesium turnings (24 grams) are treated successively with allyl bromide (10 grams) and acetaldehyde (4 grams). On treating the product in the usual way, Δ^{α}-penten-δ-ol is obtained as a colourless liquid, b. p. 115—116°, D^{20} 0·840, n_D^{20} 1·425; the *acetyl* derivative has b. p. 132—135°. Phosphorus pentachloride converts it into a mixture of $\beta\delta$-dichloropentane and *δ-chloro-Δ^{α}-pentene*, b. p. 97—100°. W. O. W.

$\alpha\epsilon$-Dimethoxy-Δ^{β}-pentinene and its Hydrogenation. ROBERT LESPIEAU (*Compt. rend.*, 1912, **154**, 886—888).—*$\alpha\epsilon$-Dimethoxy-Δ^{β}-pentinene*, $OMe{\cdot}CH_2{\cdot}C{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, prepared from the magnesium derivative of δ-methoxy-Δ^{α}-butinene (Abstr., 1907, i, 581), has b. p. 176—177°/760 mm., D^{16} 0·9385, n_D^{16} 1·442. By addition of bromine it yields *$\beta\gamma$-dibromo-$\alpha\epsilon$-dimethoxy-Δ^{β}-pentene*, b. p. 132—133°/15 mm. Hydrogenation in presence of platinum black leads to the formation of $\alpha\epsilon$-dimethoxypentane and α-methoxypentane, the latter being formed with loss of methyl alcohol. W. O. W.

Hydrolysis and Constitution of Lecithin. FERNAND MALENGREAU and GEORGES PRIGENT (*Zeitsch. physiol. Chem.*, 1912, **77**, 107—120. Compare Abstr., 1911, ii, 795).—Lecithin is hydrolysed by acids in the same manner as glycerolphosphoric acid; fatty acid and phosphoric acid are eliminated simultaneously, although the fatty acid is split off much more quickly, the difference being the more marked as the catalytic activity of the acid increases.

The choline group in lecithin does not behave as if it were an ester group attached to phosphoric acid. It is rapidly eliminated at the same rate as the fatty acids.

After two hours' heating of lecithin-cadmium chloride with *N*/10-sulphuric acid, hydrolysis is incomplete; nearly all the choline has been eliminated, but only 3·9% of the glycerolphosphoric acid has been resolved. As heating is continued, the glycerolphosphoric acid is progressively hydrolysed, and after seventy-two hours' heating this has occurred to about the extent of three-fourths.

With *N*/10-hydrochloric acid, the fatty acids are completely eliminated from lecithin in eight hours, but only 12·8% of the glycerolphosphoric acid is hydrolysed. E. F. A.

Action of Phosphorus Trichloride on Organic Acids: Monoacetylphosphorous Acid. BENJAMIN T. BROOKE (*J. Amer. Chem. Soc.*, 1912, **34**, 492—499).—The reaction between phosphorus trichloride and acetic acid is represented in certain text-books by the equation (1) $3CH_3\cdot CO_2H + 2PCl_3 \longrightarrow 3CH_3\cdot COCl + P_2O_3 + 3HCl$, and in others by the equation (2) $3CH_3\cdot CO_2H + PCl_3 \longrightarrow 3CH_3\cdot COCl + P(OH)_3$. A study of this reaction has now been made, and has shown that equation (2) is correct, whilst equation (1), indicating the formation of phosphorous oxide, is entirely wrong.

Two secondary reactions take place, the more important of which is expressed thus: $CH_3\cdot CO_2H + CH_3\cdot COCl \rightleftarrows (CH_3\cdot CO)_2O + HCl$. It has been found that when the preparation is carried out in the usual way under a reflux condenser, the hydrogen chloride required to convert the acetic anhydride into the chloride escapes from the reaction mixture. If, however, the mixture of glacial acetic acid and phosphorus trichloride is left at 18° for six hours under a slight pressure (equivalent to 10 cm. of concentrated sulphuric acid), only a small amount of hydrogen chloride escapes, and the formation of acetic anhydride is almost completely obviated.

The other secondary reaction results in the formation of acetylphosphorous acid, thus: $P(OH)_3 + CH_3\cdot COCl = P(OH)_2\cdot OAc + HCl$. *Acetylphosphorous acid* can be prepared in a pure state by adding 40 c.c. of acetic anhydride to 5 grams of phosphorous acid at the ordinary temperature, treating the mixture with 10 c.c. of acetyl chloride, and warming to 50°. The compound separates in white crystals, and, after the supernatant liquid has been decanted, is washed with ether and dried under a pressure of 10 mm.

When acetyl chloride is prepared by using the quantities of acetic acid and phosphorus trichloride indicated by equation (1), phosphorous oxide is not produced, but the residue consists of phosphorous acid and a small amount of the acetyl derivative. The phosphorus trichloride in excess of that required by equation (2) can be recovered.

The quantity of hydrogen chloride evolved by the action of acetyl chloride on phosphorous acid has been estimated, and the results indicate that a diacetyl derivative may possibly be formed, although it could not be isolated. E. G.

Ethyl Dinitroacetate. ANDRÉ WAHL (*Ann. Chim. Phys.*, 1912, [viii], **25**, 421—430).—A more detailed account of work already published (Abstr., 1903, i, 225; 1904, i, 795). In the action of nitric acid on ethyl hydrogen malonate there is formed, in addition to ethyl dinitroacetate, some ethyl furoxandicarboxylate. In general, ethyl dinitroacetate is formed by the action of nitric acid on compounds of the following types: $CHR:CH\cdot CO_2Et$; $CRR:CH\cdot CO_2Et$; $CHR:C(COMe)\cdot CO_2Et$. Ethyl dinitroacetate decomposes slowly when kept, or at once when heated, forming nitric acid and ethyl furoxandicarboxylate (compare Jovitschitsch, Abstr., 1902, i, 202).

T. A. H.

Action of Concentrated Sulphuric Acid on Trilaurin. B. W. VAN ELDIK THIEME (*J. pr. Chem.*, 1912, [ii], **85**, 284—307).—The preparation of mono- and di-glycerides by the action of alkali salts of aliphatic acids on glycerol mono- and di-chlorohydrins (Guth, *Diss.*, Rostock, 1902; Krafft, Abstr., 1904, i, 136) is not recommended by the author, as it is found that a mixture of glycerides is produced; thus, sodium laurate and glycerol α-monochlorohydrin yield a mixture of monolaurin, dilaurin, and trilaurin, whilst with glycerol αγ-dichlorohydrin the product consists mainly of dilaurin and trilaurin. An explanation of these results was obtained from the behaviour of glycerol towards sodium laurate; when heated at 100°, a mixture of these substances becomes alkaline, owing to the formation of sodium hydroxide, partial esterification taking place simultaneously:

$$C_3H_5(OH)_3 + C_{11}H_{23}\cdot CO_2Na = C_{11}H_{23}\cdot CO_2\cdot C_3H_5(OH)_2 + NaOH.$$

A similar esterification, resulting in the formation of a mixture of glycerides, occurs with the glycerol chlorohydrins; the production of monolaurin, αβ- and αγ-dilaurin, and trilaurin from glycerol αγ-dichlorohydrin is represented in the following scheme ($R = C_{11}H_{23}\cdot CO$).

$$OH\cdot CH(CH_2Cl)_2 \xrightarrow{2NaOR} OH\cdot CH(CH_2\cdot OR)_2 \xrightarrow{NaOR} C_3H_5(OR)_3 + NaOH$$

$$OH\cdot CH(CH_2Cl)_2 \xrightarrow[NaOH]{} OH\cdot CH_2\cdot CH(OH)\cdot CH_2Cl \xrightarrow[NaOR]{}$$

$$OH\cdot CH_2\cdot CH(OH)\cdot CH\cdot OR \text{ and } OH\cdot CH_2\cdot CH(OR)\cdot CH_2\cdot OR.$$

These results also afford an explanation of the widely divergent values given in the literature for the m. p.'s of mono- and di-glycerides. β-Monolaurin (compare Grün and Skopnik, Abstr., 1910, i, 356) is obtained in a pure condition as follows: glycerol αγ-dichlorohydrin is converted by means of chlorosulphonic acid into $SO_3H\cdot O\cdot CH(CH_2Cl)_2$, which reacts with lauric acid at 45°, yielding *β-lauro-αγ-dichlorohydrin*, $C_{11}H_{23}\cdot CO_2\cdot CH(CH_2Cl)_2$, a pale yellow liquid, b. p. 180—181°/4 mm.; this is transformed into the corresponding *iodohydrin* by means of sodium iodide in alcoholic solution, the iodohydrin heated with silver nitrite, and the resulting ester of nitrous acid hydrolysed with hydrochloric acid. β-Monolaurin has m. p. 60·5°. α-Monolaurin, prepared from αβ-dibromohydrin in a similar manner, has m. p. 58·9°; Grün and Skopnik (*loc. cit.*) give 52°.

α-Lauro-βγ-dibromohydrin has b. p. 197—198°/3 mm.

αβ-Dilauro-γ-chlorohydrin, prepared by the successive action of chlorosulphonic acid and lauric acid on glycerol α-chlorohydrin, has

b. p. 185—195°/5 mm., m. p. 30°; Grün and Schacht (Abstr., 1907, i, 462) give 24°. It is converted by the method described above into *αβ-dilaurin*, $OH\cdot C_3H_5(O\cdot CO\cdot C_{11}H_{23})_2$, m. p. 56·3°.

αα-Dilaurin, obtained together with αβ-dilaurin by heating glycerol with lauric acid, is an oil; the product obtained by Grün and Schacht (*loc. cit.*) by the interaction of sodium laurate and αα-dichlorohydrin, and described by them as αα-dilaurin, consists mainly of αβ-dilaurin and trilaurin.

Lauric acid forms with sulphuric acid a crystalline *compound* of the composition $C_{11}H_{23}\cdot CO_2H,1\frac{1}{2}H_2SO_4$; a similar *compound* is also formed from β-lauro-αγ-dichlorohydrin.

The action of strong sulphuric acid on trilaurin has also been studied. It is found that an additive compound is first produced, which then undergoes decomposition, the lauryl groups being replaced by SO_3H. By partly hydrolysing the product, β-monolaurin and αβ-dilaurin, together with a small amount of αα-dilaurin, were obtained. For complete decomposition of trilaurin into glyceryltrisulphuric acid, a large excess of sulphuric acid and a low temperature are necessary.

The first product of the decomposition, *αβ-dilaurosulphuric acid*, has been isolated in the form of its *potassium* salt,

$$SO_3K\cdot O\cdot C_3H_5(O\cdot COC_{11}H_{23})_2.$$

Glyceroltrisulphuric acid is not readily hydrolysed by water to glycerol and sulphuric acid as stated by Klason (*J. pr. Chem.*, 1879, [ii], 20, 1); glycerolmonosulphuric acid is produced, which is readily isolated in the form of its *barium* salt, and is hydrolysed by water only after prolonged boiling. F. B.

Ethyl γ-Ethoxyacetoacetate. MARCEL SOMMELET (*Compt. rend.*, 1912, **154**, 706—708).—Although ethyl acetate reacts with ethyl bromoacetate in presence of zinc to give only a trace of ketone, yet ethyl ethoxyacetate under the same conditions readily forms ethyl γ-ethoxyacetoacetate, $OEt\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2Et$, b. p. 105—106°/11 mm., 116—117°/20 mm. When freshly prepared, this substance is colourless, but rapidly alters on exposure to air. An alcoholic solution gives a bright red coloration with ferric chloride. The *copper* salt crystallises in green needles, m. p. 145—146°. Hydrazine hydrate forms 3-*ethoxymethylpyrazolone*, $C_6H_{10}O_2N_2$, m. p. 148—149·5°. The *sodium* salt reacts with benzyl chloride, giving a mixture of mono- and di-benzyl derivatives.

Ethyl γ-ethoxy-α-benzylacetoacetate, $OEt\cdot CH_2\cdot CO\cdot CH(CH_2Ph)\cdot CO_2Et$, b. p. 185—187°/14 mm., forms a *pyrazolone*, m. p. 119—120°, and on hydrolysis yields *δ-ethoxy-α-phenylbutan-γ-one*,

$$CH_2Ph\cdot CH_2\cdot CO\cdot CH_2\cdot OEt,$$

b. p. 157°/19—20 mm. (*semicarbazone*, m. p. 103—105°). *Ethyl γ-ethoxy-αα-dibenzylacetoacetate* is an oil, b. p. 243—247°/14 mm. W. O. W.

The Action of Ammonium Cyanide (Potassium Cyanide and Ammonium Chloride) on Chlorinated Aldehydes. KARL RASKE (*Ber.*, 1912, **45**, 725—734).—When an ethereal solution of chloroacetaldehyde is shaken with an aqueous solution of ammonium chloride

and potassium cyanide and the product treated with hydrochloric acid, β-chlorolactic acid is formed. When β-chloropropaldehyde is similarly treated, *γ-chloro-α-hydroxybutyric acid*, m. p. 58°, is obtained. Its *ammonium* and *silver* salts were examined. When its aqueous solution is boiled, or the solid acid preserved at the ordinary temperature, the *lactone* of $\alpha\gamma$-dihydroxybutyric acid is formed. The *ammonium* and *calcium* salts of the latter acid were investigated.

Chloralacetamide, when acted on successively by hydrocyanic and hydrochloric acids, yielded a *product*, the analyses of which agreed with the formula $CCl_3{\cdot}CH(NHAc){\cdot}CO{\cdot}NH_2,H_2O$, m. p. 88—89°. This appears, however, to be a compound of trichlorolactamide and acetamide, since it is readily resolved into these substances by the action of hydrochloric acid, and it can also be obtained by crystallising a mixture of these substances from chloroform or benzene. Attempts to obtain pure crystalline compounds of trichlorolactamide with benzamide, formamide, and pyridine respectively were unsuccessful. H. W.

Cystine. JULIUS MAUTHNER (*Zeitsch. physiol. Chem.*, 1912, **78**, 28—36).—The cystine obtained from a case of cystinuria had $[\alpha]_D - 205{\cdot}28°$. By treatment with ammonia and zinc dust at the ordinary temperature the sulphur was removed and about half the theoretical quantity of alanine was obtained. This proved to be *dl*-alanine.

Cystine interacts with potassium cyanide, forming *α-amino-β-thiocyanopropionic acid*, $SCN{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$; this crystallises in short, stout, lustrous prisms, also in flat prisms and six-sided platelets. On heating it becomes brown at 180°, m. p. 220° (decomp.), $[\alpha]_D^{18} - 83{\cdot}17°$. The *copper* salt separates in rosettes of microscopic platelets, or when quickly precipitated in tiny needles; the *hydrochloride* forms long prisms and needles. E. F. A.

Dichloroacetaldehyde and the Formation of Vinyl Acetates from Bromoacetaldehydes. BRUNO MYLO (*Ber.*, 1912, **45**, 645—651).—*β-Bromovinyl acetate*, $CHBr{:}CH{\cdot}OAc$, b. p. 146—149°, is obtained by treating dibromoacetaldehyde (1 mol.) and acetyl bromide (about 5 mols.) with finely divided copper (1 atom) and heating the mixture at the b. p. for sixteen hours. *$\alpha\beta\beta$-Tribromoethyl acetate*, $CHBr_2{\cdot}CHBr{\cdot}OAc$, b. p. 114—117°/15·5 mm., is prepared by heating equal molecular quantities of dibromoacetaldehyde and acetyl bromide. *$\beta\beta$-Dibromovinyl acetate*, $CBr_2{:}CH{\cdot}OAc$, b. p. 70—71·5°/7 mm., is prepared from bromal, acetyl bromide, and finely divided copper. Equal molecular quantities of dichloroacetaldehyde and acetaldehyde are converted, after the addition of a little aqueous zinc chloride, into *dichlorotrimethyltrioxin*, $CHCl_2{\cdot}CH{<}\begin{matrix}O{\cdot}CHMe\\O{\cdot}CHMe\end{matrix}{>}O$, m. p. 73—74·5°, colourless prisms, and *bisdichlorotrimethyltrioxin*, $CHMe{<}\begin{matrix}O{\cdot}CH(CHCl_2)\\O{\cdot}CH(CHCl_2)\end{matrix}{>}O$, m. p. 53—54·5°, tufted needles; both have an intense odour, somewhat resembling that of paraldehyde. C. S.

Hydrolysis of Carbohydratephosphoric Acid Esters. HANS VON EULER and YNGVE FUNKE (*Zeitsch. physiol. Chem.*, 1912, 77, 488—496).—Sodium hexosephosphate is not hydrolysed by trypsin, pepsin, defibrinated blood, or by a kidney extract. When fed to a rabbit, three-quarters of the hexosephosphate were hydrolysed.

E. F. A.

Specific Rotatory Power of Lævulose. BERNHARD TOLLENS (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 360—361).—Herzfeld and Winter (Abstr., 1886, 438) have found values between $-71°$ and $-77°$ for the rotatory power of lævulose. It is pointed out that both observers used lævulose syrups, and omitted to allow for the moisture in these when calculating the experimental results. When recalculated a value of $-92°$ to $-93°$ is obtained in each case, agreeing with that generally accepted. E. F. A.

Saccharification of Starch by Dilute Acids. AUGUSTE FERNBACH and MARCEL SCHOEN (*Bull. Soc. chim.*, 1912, [iv], 11, 303—308). —The balance of existing evidence is in favour of the view that whilst malt diastase hydrolyses starch to dextrins and maltose, dilute acids convert it into dextrose, although in recent years Weber and Macpherson (Abstr., 1895, ii, 296) and others have found maltose in the commercial glucose prepared by acid hydrolysis of starch. The authors have prepared phenylosazones from the products obtained by the hydrolysis of starch mucilage under pressure with hydrochloric acid, oxalic acid, and sulphuric acid, and in each case have obtained notable quantities of maltosazone, which was identified by its crystalline form and melting point. The latter was generally low, owing to the difficulty of freeing the substance from small quantities of dextrins (compare Grueters, *Compt. rend.*, 1890, **110**, 1204). T. A. H.

Humic Acid of Sphagnum Peat. SVEN ODÉN (*Ber.*, 1912, 45, 651—660).—The object of the research is to ascertain whether or not the non-colloidal alkali compounds obtained by the action of alkalis on the humous substances of sphagnum peat are true salts. Reasons are stated for the belief that such alkali compounds are non-colloidal. The preparation from peat of a solution of ammonium humate free from colloids is described. By ultramicroscopical examination, the solution exhibits very feeble internal luminescence, which is due probably to the high molecular weight of ammonium humate (compare Lobry de Bruyn, Abstr., 1904, ii, 470). By suitable treatment with hydrochloric acid and centrifugalising, the free humic acid can be isolated. The fact that the electrical conductivity of $0·182 N$-ammonia is increased by the addition of a suspension of humic acid, shows that the latter is a true acid, and forms an ammonium salt which is electrolytically dissociated. The equivalent weight of the acid is about 339 as determined by Kohlrausch's conductivity method; $0·00520 N$-sodium hydroxide is treated with successive small quantities of a suspension of humic acid (containing 0·0042 gram per c.c.) until the equivalent conductivity reaches a minimal value. As determined by the analysis of the calcium salt, the equivalent weight of humic acid is 345. The

variation with the dilution of the equivalent conductivity of solutions of sodium humate indicates that humic acid is tribasic.

When humic acid is heated at 100°, the gelatinous mass loses water and is changed to a hard, brittle substance, which forms a black, glistening powder. This modification does not form a suspension in water, and is not directly soluble in alkalis. By the prolonged action of alkalis, however, it swells and partly dissolves as the brown alkali humate; the change is by no means complete, even after forty-six days. C. S.

Coal and Carbonised Residues. EDUARD DONATH and FRITZ BRÄUNLICH (*Chem. Zeit.*, 1912, **36**, 373—376).—The study of coals by means of the reaction with dilute nitric acid (*ibid.*, 1904, **28**, 180) has now been extended to include other reagents. Fusion with alkali hydroxide at 250° and extraction with water gives dark brown solutions with brown coal, charcoal, and carbonised organic material, and much of the coloured matter is precipitated by acids. True coal, coke, graphite, and acetylene soot yield colourless solutions. Brown coals are almost completely converted into humic acids, and these acids may be separated into two fractions, one of which is completely soluble in the concentrated alkali (I), whilst the second remains insoluble, but is dissolved by very dilute alkali hydroxide (II). After precipitation with acid, the two substances may be distinguished by their behaviour towards a 10% solution of ammonium carbonate, in which (I) is completely soluble and (II) insoluble. The acid (I) is insoluble in cold water, whilst (II) yields a dark brown solution. True coal may be rendered soluble by repeated fusion with alkali at 400°.

The humic acids (I) from brown coal are mixed with oxalic acid and an acid which sublimes at 300°, and also with a crystalline substance which gives a red coloration with ferric chloride. A fatty acid is also present. If ferric oxide is added to the alkali fusion, a clear solution is obtained with water, and acids no longer produce a precipitate. Much oxalic acid is present, as well as substances which give a coloration with ferric chloride.

A mixture of equal volumes of concentrated nitric and sulphuric acids reacts violently with brown coal and wood, but only slowly with coal. Those materials which yield humic acids with alkali are converted by the acid mixture into substances soluble in acetone or alcohol, and this furnishes a ready means of distinguishing between the two classes of coal. C. H. D.

Alkylation of Amino-acids with Alkyl Sulphates. JOH. NOVÁK (*Ber.*, 1912, **45**, 834—850).—An endeavour to improve the esterification method for the estimation of amino-acids. Methyl sulphate applied in the cold with an aqueous solution of an alkali gives, in general, excellent yields of a product methylated at both the carboxyl group and the nitrogen atom. The analogous reaction with ethyl sulphate is far from complete even when assisted by warming. The reaction product, after neutralisation with sulphuric acid, is evaporated to a syrup and extracted with alcohol; after again evaporating, warming with dilute hydrochloric acid to decompose any

alkylsulphuric acid, and then removing sulphuric acid by barium chloride, the hydrochloride of the amino-ester is extracted with alcohol and examined by conversion into various derivatives.

Glycine gave with methyl sulphate a 93% yield of betaine hydrochloride, together with a small quantity of the methyl ester of betaine hydrochloride. With ethyl sulphate, triethylbetaine was obtained (platinichloride, m. p. 217—218·5° corr.), together with diethylaminoacetic acid; the latter results from the hydrolysis of its ethyl ester (platinichloride, tablets, m. p. 140—142° corr.), which is also produced.

dl-Alanine with methyl sulphate produced only methylbetaine (α-trimethylpropiobetaine) (83·6% theory), the platinichloride of which melts at 210—212° (corr.). No betaine compound was obtained with ethyl sulphate, the products being α-diethylaminopropionic acid (copper salt, violet-red leaflets), the corresponding ethyl ester, b. p. 86°/18 mm. (platinichloride, tablets, m. p. 114—116° corr.), and a little α-ethylaminopropionic acid (the copper salt was prepared).

dl-Leucine on methylation gave 87% of the theoretical yield of the *betaine* of *α-trimethylammonium*iso*hexoic acid*; *platinichloride*, leaflets, m. p. 217—218° (corr.); *aurichloride*, leaflets, m. p. 164—165° (corr.). Ethyl sulphate left most of the leucine unaffected, but a little α-ethylamino*iso*butylacetic acid was obtained (copper salt, violet powder).

dl-Phenylalanine was methylated to the *betaine* of *α-trimethylammoniumphenylpropionic acid*; *platinichloride*, tablets, m. p. 195·5—196·5° (corr.); *aurichloride*, leaflets, m. p. 93—94° (corr.). The yield was 96%.

l-Aspartic acid, when methylation was attempted, gave a practically quantitative yield of fumaric acid, the rest of the molecule appearing as a mixture of tetramethylammonium chloride, trimethylamine, and dimethylamine. In the treatment with ethyl sulphate, a small amount of fumaric acid and diethylamine was obtained.

d-Glutamic acid gave on methylation a 92% yield of a pentamethyl derivative, probably the *chloride* of the *dimethyl* ester of N-*trimethylglutamic acid* ($CO_2Me\cdot CH_2\cdot CH_2\cdot CH\cdot NMe_3Cl\cdot CO_2Me$); *platinichloride*, needles, m. p. 201° (decomp.); *aurichloride*, needles, m. p. 125—128°. A small quantity of a dimethyl derivative, probably N-*dimethylglutamic acid*, was also obtained (aurichloride, leaflets). The action of ethyl sulphate on glutamic acid gave no satisfactory result.

D. F. T.

Polypeptides Containing *d*-Aminobutyric Acid. Emil Abderhalden and Hsing Lang Chang (*Zeitsch. physiol. Chem.*, 1912, **77**, 471—487. Compare Abderhalden, Chang and Wurm, Abstr., 1911, i, 526).—Several new dipeptides have been prepared containing *d*-aminobutyric acid, also three of the possible tripeptides containing glycine, alanine, and aminobutyric acid. Attention is called to the great alteration in physical and biochemical properties caused by the alteration in the order in which these three units are united.

Glycyl-*dl*-aminobutyric anhydride, prepared from glycyl-*dl*-aminobutyric acid, crystallises in rhombic plates, m. p. 238°, and is identical with the anhydride prepared from α-aminobutyrylglycine (Fischer and Raske, Abstr., 1906, i, 457).

l-Aminobutyric acid is converted by nitrosyl bromide into *d*-α-bromobutyric acid, $[\alpha]_D^{20}$ $+15\cdot43°$. On treatment with ammonia partly racemised *d*-α-aminobutyric acid is obtained.

d-Bromobutyryl chloride, prepared by the action of thionyl chloride on the acid, has b. p. 65—69°/15 mm.

d-*Bromobutyryl-glycyl*-d-*aminobutyric acid*, prepared from glycyl-*d*-aminobutyric acid and *d*-bromobutyryl chloride, crystallises in very minute needles, m. p. 141° (corr.), $[\alpha]_D^{20}$ $+5\cdot55°$. When set aside with 25% ammonia, d-*aminobutyryl-glycyl*-d-*aminobutyric acid* is formed; it has m. p. 241° (decomp.), $[\alpha]_D^{20}$ $+12\cdot75°$.

d-*Bromobutyryl-glycyl*-d-*alanine* sinters at 80°, m. p. 148°, $[\alpha]_D^{20}$ $-21\cdot32°$. d-*Aminobutyryl-glycyl*-d-*alanine* reacts acid with litmus in aqueous solution; it has m. p. 239° (corr.), $[\alpha]_D^{20}$ $-7\cdot8°$.

d-*Bromobutyryl*-d-*alanine* crystallises in cubes or in teeth-like branched platelets, which soften at 112° (corr.), m. p. 132° (corr.), $[\alpha]_D^{20}$ $-20\cdot08°$.

d-*Aminobutyryl*-d-*alanine* has m. p. 266° (corr.), $[\alpha]_D^{20}$ $-12\cdot55°$.

Chloroacetyl-d-*aminobutyryl*-d-*alanine* crystallises in needles, m. p. 195° (corr.), $[\alpha]_D^{20}$ $-61\cdot94°$. *Glycyl*-d-*aminobutyryl*-d-*alanine* is neutral to litmus in aqueous solution, m. p. 247° (corr.), $[\alpha]_D^{20}$ $-76\cdot62°$.

d-*Bromobutyrylglycine* has m. p. 93° (corr.), $[\alpha]_D^{20}$ $+32\cdot44°$. d-*Aminobutyrylglycine* is a crystalline powder, m. p. 226° (corr.), $[\alpha]_D^{20}$ $+26\cdot83°$.

d-*Bromopropionyl*-d-*aminobutyrylglycine* separates in long needles, m. p. 166° (corr.), $[\alpha]_D^{20}$ $-12\cdot83°$. d-*Alanyl*-d-*aminobutyrylglycine* has m. p. 214° (corr.), $[\alpha]_D^{20}$ $+13\cdot86°$.

Glycyl-*d*-aminobutyric acid has $[\alpha]_D^{20}$ $-20\cdot33°$. E. F. A.

Electrochemical Reductions. I. Reduction of Primary Nitroamines into Hydrazines. H. J. Backer (*Rec. trav. chim.*, 1912, **31**, 1—29).—The author has reduced a number of primary nitroamines by electrical methods, using a cathode of tin or of copper coated with tin (compare Boehringer & Söhne, Abstr., 1906, i, 637). The cathode liquid was varied according to the stability of the substances worked with, using either dilute sulphuric or acetic acids or a mixture of the two, a solution of sodium sulphate, or as an alkaline medium a solution of sodium carbonate. The anode liquid was sulphuric acid (20%) for acid reductions, and a saturated solution of sodium carbonate for alkaline reductions. The hydrazines obtained by the reductions invariably were characterised by preparing condensation products with aldehydes.

Methyl nitrourethane is best reduced in a dilute solution of acetic acid containing sodium acetate, methyl hydrazinecarboxylate hydrochloride being obtained (yield 88%), and characterised by its benzylidene derivative (compare Diels and Fritzsche, Abstr., 1911, i, 957). The p-*nitrobenzylidene* derivative,

$$CO_2Me\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot NO_2,$$

crystallises in pale yellow needles, m. p. 212°. By reduction in alkaline solution, contrary to expectation, free hydrazine itself is formed. Ethyl nitrourethane gives a yield of 70% on similar reduction in acid solution.

Nitrocarbamide is best reduced in a mixture of dilute acetic and

sulphuric acids, the semicarbazide hydrochloride being subsequently obtained to the extent of 74% of theory (compare Holroyd, Trans., 1901, **79**, 1326). By condensation with pyruvic acid, the *semicarbazone*, $NH_2 \cdot CO \cdot NH \cdot N \colon CMe \cdot CO_2H$, is obtained in white needles, which melt and decompose at 200°. From it a *potassium* and *barium* salt have been prepared. W. G.

Constitution of the Fulminuric Acids. III. CELSIO ULPIANI (*Gazzetta*, 1912, **42**, i, 209—227).—The author calls attention to two papers (Abstr., 1905, i, 750; *Rend. Soc. Chim. Roma*, 26th Nov., 1905) in which he described previously to the work of Jovitschitsch (Abstr., 1906, i, 732) the gradual decomposition of ethyl furoxandicarboxylate, although with results differing substantially from those of Jovitschitsch. In the present paper an account is given of the action of boiling water on ethyl furoxandicarboxylate (previously recorded in the second of the papers above-mentioned), and the results so obtained are discussed in connexion with those of Wieland (Abstr., 1909, i, 610), who observed a different series of reactions when the hydrolysis was effected with barium hydroxide.

When ethyl furoxandicarboxylate is boiled with water for four or five days, and the aqueous liquid then neutralised with ammonia, *ethyl ammonionitrocyanoacetate*, $CO_2Et \cdot C(CN) \colon NO \cdot OH, NH_3$, is obtained in crystalline form after evaporation. When potassium carbonate is used instead of ammonia, the potassium derivative is obtained, and is identical with that of Conrad and Schulze (Abstr., 1909, i, 211). The *silver* derivative, $C_5H_5O_4N_2Ag$, crystallises in heavy needles. When it is treated with hydrogen sulphide and filtered, the filtrate yields on evaporation in a vacuum, transparent, prismatic crystals, which consist probably of impure *ethyl nitrocyanoacetate*. On reduction with sodium amalgam, ethyl ammonionitrocyanoacetate yields the sodium oximinocyanoacetate, whilst when it is treated in alcoholic solution with hydrogen chloride, the ammonium salt of ethyl nitromalonate is produced. This shows that the middle carbon atom of the product obtained by the author by the destruction of ethyl furoxandicarboxylate is linked with a nitro-group, whilst in Wieland's products there is an oximino-group. An aqueous solution of ethyl ammonionitrocyanoacetate treated with an ammoniacal copper solution slowly deposits the compound $(C_3H_2O_3N_3)_2Cu, 4NH_3$, identical with that obtained from ammoniacal copper solutions of ammonium fulminurate (compare Conrad and Schulze, *loc. cit.*). Saponification of ethyl ammonionitrocyanoacetate with barium hydroxide yields the *barium* derivative, $C_3O_4N_2Ba, 2H_2O$, but it is not possible to isolate the free acid, because it decomposes quantitatively in solution, forming nitroacetonitrile and carbon dioxide. The *ammonium* salt of nitroacetonitrile, $C_2N_2O_2H_2, NH_3$, has m. p. about 135°.

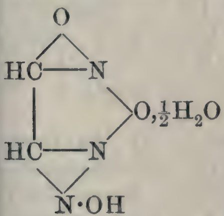
R. V. S.

Constitution of the Fulminuric Acids. IV. CELSIO ULPIANI (*Gazzetta*, 1912, **42**, i, 243—263).—The paper records attempts which have been made to prepare (or to ascertain the structure of) some of

the seven different substances $C_2H_2O_2N_2$, which have at least one oxygen atom linked with nitrogen.

By the action of boiling water on ethyl furoxandicarboxylate the author obtained (compare preceding abstract) nitrocyanoacetic acid (of which the constitution was established by Conrad and Schulze, Abstr., 1909, i, 211) and nitroacetonitrile (of which the constitution was settled by Steinkopf and Bohrmann, Abstr., 1908, i, 327). The substance of m. p. 40° described by Steiner (Trans., 1876, ii, 288) as nitroacetonitrile, the author finds to have the composition $C_4O_2N_4$, and to be, consequently, *furoxandicarboxylonitrile*, $\begin{matrix} CN\cdot C{:}NO \\ \vert \quad\ \vert \\ CN\cdot C{:}NO \end{matrix}$

[With A. De Dominicis.]—From the oxidation of glyoxime with sodium hypochlorite or with concentrated nitric acid, no individual product could be isolated. Oxidation of glyoxime with permanganate yields a *compound* (C 25·91%, H 4·08%, N 30·64%), which crystallises in needles and decomposes at 97°. When glyoxime is oxidised with nitrogen peroxide in ethereal solution, a yellow, crystalline *substance*, $C_2H_3O_3N_3,\frac{1}{2}H_2O$, is obtained; it has m. p. 104°. It forms an *ammonium* salt, $C_2H_3O_3N_3\cdot NH_3,\frac{1}{2}H_2O$. For this substance of m. p. 104° the annexed formula is suggested.



[With N. Sciacca.]—The interaction of equimolecular quantities of ethyl cyanocarboxylate and hydroxylamine in alcoholic solution yields a crystalline substance, $C_4H_8O_3N_2$, m. p. 99—100°. It gives a green precipitate with copper acetate, and an intense reddish-violet coloration with ferric chloride. The substance is assigned the structure of the *ethyl* ester of *oxalmonoamido-oxime*, $CO_2Et\cdot C({:}N\cdot OH)\cdot NH_2$. When it is saponified with sodium hydroxide, a crystalline substance, m. p. 141° (decomp.), is obtained, which is probably *oxalmonoamido-oxime*. The *silver* salt, $C_2H_3O_3N_2Ag$, forms acicular crystals. R. V. S.

Sodium Pentacyanohydrazinoferrite [Hydrazinoferropentacyanide]. E. Biesalski and Otto Hauser (*Zeitsch. anorg. Chem.*, 1912, **74**, 384—388).—If a concentrated solution of 6 grams of hydrazine hydrate is added, drop by drop, to an ice-cold alkaline solution of 12 grams of sodium nitroprusside in ethyl and methyl alcohol, a yellow, crystalline precipitate is obtained, which is washed with alcohol and ether and dried over sulphuric acid, and has the composition $Na_3N_2H_4(CN)_5,H_2O$. It gives the characteristic reaction of ferropentacyanides, a red coloration when boiled with hydroxylamine. It readily decomposes, becoming green and evolving cyanogen.

At least one more cyanogen group may be replaced by using an excess of hydrazine. Similar reactions occur, but less readily, with phenylhydrazine, ethylamine, and diethylamine (compare Hofmann, Abstr., 1900, i, 591). C. H. D.

New Silicanes. Artur Bygdén (*Ber.*, 1912, **45**, 707—713. Compare Abstr., 1911, i, 845).—The author has extended his work on

tetra-alkylsilicanes, and has prepared compounds containing 9, 10, and 11 atoms of carbon, and a derivative of silicoethane, as well as silicanes containing the phenyl group. The following substances are described:

Triethyl-n-*propylsilicane*, b. p. 172·8—173·2° (corr.)/761·4 mm., D_4^{15} 0·775, from trichloro-*n*-propylsilicane and magnesium methyl bromide (4·5 mols.); *triethyl*-n-*butylsilicane*, b. p. 190·6—191·6°/762·2 mm., D_4^{15} 0·782, from trichlorobutylsilicane and magnesium ethyl bromide (4·2 mols.); *triethylisobutylsilicane*, b. p. 187·0—187·2° (corr.)/762 mm., D_4^{15} 0·784, from trichloro*iso*butylsilicane and magnesium ethyl bromide (4·5 mols.); *triethylisoamylsilicane*, b. p. 204·6—205·6° (corr.)/757·3 mm., D_4^{15} 0·785, from trichloro*iso*amylsilicane and magnesium ethyl bromide (4·5 mols.).

Hexamethylsilicoethane, Si_2Me_6, prepared from silicon hexachloride and magnesium methyl bromide (6·2 mols.), has b. p. 112—114° (corr.)/756·9 mm., m. p. 12·5—14°.

Trichlorophenylsilicane, isolated from the product obtained by the gradual addition of magnesium phenyl bromide to a solution of silicon tetrachloride in ether, has b. p. 200·5—201·5° (corr.)/740·4 mm., whereas Ladenburg (Abstr., 1873, 1026) found 197°. Magnesium methyl bromide (3·3 mols.) and magnesium ethyl bromide (4·2 mols.) convert it respectively into *phenyltrimethylsilicane*, b. p. 171·5—171·7° (corr.)/759·4 mm., D_4^{15} 0·873, and *phenyltriethylsilicane*, b. p. 238·2—238·4° (corr.)/763·1 mm., D_4^{15} 0·894.

An attempt to prepare dichlorophenylethylsilicane by the interaction of magnesium ethyl bromide (1·1 mols.), and trichlorophenylsilicane was not completely successful (compare Kipping, Trans., 1907, 91, 215), but the product so obtained, when acted on by magnesium methyl bromide (2·3 mols.), yielded *phenyldimethylethylsilicane*, b. p. 197·6—198·6° (corr.)/758·7 mm., D_4^{15} 0·881.

Benzyltrimethylsilicane, prepared from trichlorobenzylsilicane and magnesium methyl bromide (3·3 mols.), has b. p. 191·2—191·4° (corr.)/759·5 mm., D_4^{15} 0·872. H. W.

Proposals for a Nomenclature of Heterocyclic Substances and its Extension to Cyclic Substances in General and to Acyclic Compounds. AUGUSTE BÉHAL (*Bull. Soc. chim.*, 1912, [iv], 11, 264—275).—The nomenclature proposed is a literal rendering of formulæ without reference to the functions of the characteristic groups in the substance, and it is suggested that it would be especially useful for indexing purposes.

Greek prefixes are to be used to indicate the number of links in a closed chain, and the nature of the links will be indicated by the words oxo, azo, thio for rings containing O, N or S, or oxonio, azonio, sulphinio, etc., in the case of oxonium, azonium or sulphinium compounds. The residue :SO will be called thion, and SO_2 will be named sulphone. The names of closed saturated chains will end in -ane, and unsaturation will be indicated by the terminations -ene, -diene, -triene, etc.; thus, dihydropyrrole will be *cyclo*pentazene, and pyridine becomes *cyclo*hexazotriene. The numbering of the links composing the ring will begin with the atom of lowest atomic weight. In polyheterocyclic compounds, Latin prefixes will be used to indicate the number

of rings, and numbers appended indicating the points of attachment; thus quinoline would be bicyclo-5 : 10-decazo-1-pentene-1 : 3 : 5 : 6 : 8. The same system could be used for polyhomocyclic substances; thus anthracene would be tetracyclo-1 : 8 : 2 : 7 : 9 : 14-tetradecahexene-2 : 3 : 5 : 9 : 10 : 12. In the case of bridged rings, the linking atoms forming the bridge would be indicated by letters *a*, *b*, *c*, etc., and the position of the bridge by the numbers of the atoms in the primary ring, at which it is attached; thus pinene would be bicyclo-*a* : 6 : 4-heptene-1-trimethyl-*a* : *a* : 1. In general, the longest possible chain is to be taken as the basis of the name, and where two chains are of equal length the more complex is to be taken as a basis. The dioxide formula for quinone would be called bicyclo-*a* : *b* : 1 : 4-octodioxotriene-1 : 3 : 5, or, if preferred, the nature of the linking bridge atoms may be indicated thus: bicyclo-*a* : *b*(O.O) : 1 : 4-octo-dioxotriene-1 : 3 : 5.

The system is applied to acyclic compounds with the addition of the Geneva system of numbering atoms in side-chains, and the convention that oxygen doubly linked to carbon is to be indicated by the suffix -one; thus diethyl ether becomes pentoxane-3, the acid anhydride, $CH_3{\cdot}CHMe{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CHMe{\cdot}CH_3$, becomes octoxane-4-dione-3 : 5-dimethyl-2 : 7, and sulphonal, $CH_2Me{\cdot}SO_2{\cdot}CMe_2{\cdot}SO_2{\cdot}CH_2Me$, would be called heptadisulphone-3 : 5-dimethyl-4 : 4.

The names may be shortened by using numerals and letters in place of prefixes, thus 3C for tricyclo- and so on, different kinds of type being used for numerals and letters serving different purposes in the name, thus *β*-naphthol tetrahydride could be written 2C-1 : 6-1O-triene-2 : 4 : 6-ol-3 (bicyclo-1 : 6-decatriene-2 : 4 : 6-ol-3).

A large number of examples of the application of this system to the naming of complex substances are given in the original.

T. A. H.

$\Delta^{1:3}$-*cyclo*Hexadiene. CARL D. HARRIES (*Ber.*, 1912, **45**, 809—816. Compare Abstr., 1909, i, 218; Crossley, Trans., 1904, **85**, 1403).—The formation of *cyclo*hexene as well as *cyclo*hexadiene on elimination of hydrogen bromide from 1 : 2-dibromo*cyclo*hexane by means of quinoline is confirmed, contrary to the results of Zelinsky and Gorsky (Abstr., 1911, i, 847), by the following new investigation. When dibromo*cyclo*hexane is treated in alcoholic solution with trimethylamine, an *additive product*, $C_9H_{18}NBr$, of trimethylamine with a monobromide is obtained, m. p. 181° (decomp.). When heated, this decomposes into trimethylamine and a hydrocarbon, C_6H_8, D_{20}^{20} 0·8421, n_D^{20} 1·475. It gives an intense dark red coloration with concentrated sulphuric acid. On prolonged treatment with ozone a mixture of *mono-* and *di-ozonide* is obtained, from which, on decomposition, succindialdehyde and other products resulted.

The hydrocarbon when brominated yields a tetrabromide crystallising in thick, colourless prisms, m. p. 87—89°. On brominating the mixture of hydrocarbons obtained by the method of Zelinsky and Gorsky, two tetrabromides, m. p. 87—89° and 155—156°, possibly corresponding with *cis-* and *trans*-isomerides, as well as an oily fraction,

were obtained; the last contained 1 : 2-dibromo*cyclo*hexane, corresponding with about 25% of *cyclo*hexene in the original hydrocarbon.

E. F. A.

Indones and their Transformation Products in Sunlight. Behaviour with Ozone. MARUSSIA BAKUNIN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 379—386. Compare Bakunin and Lanis, Abstr., 1911, i, 992).—The present paper deals with 4-nitro-2-phenylindone and with the product, m. p. about 320°, obtained when it is kept in sunlight. The latter does not react with phenylhydrazine or semicarbazide. 4-Nitro-2-phenylindone, however, yields with semicarbazide a *substance*, $C_{16}H_{12}O_3N_4$, which has m. p. 210°, and crystallises in yellow needles.

The action of ozone on the nitrophenylindone and on the substance of m. p. 320° has also been investigated, the dilute ozone employed being obtained by passing oxygen through a Berthelot tube connected with an induction coil. 4-Nitro-2-phenylindone when ozonised in chloroform solution at 0° yielded (1) benzoic acid; (2) a *substance*, m. p. 128° (obtained in some experiments only); (3) a well-crystallised, stable substance, m. p. 157—158°. The last-named product reacts with phenylhydrazine, and is not affected by sodium carbonate or by boiling water. When boiled with barium hydroxide, it dissolves, and from the solution, on addition of acid, benzoic acid can be obtained, and also a *substance*, m. p. 136—137°. The substance of m. p. 157° is assigned the constitution of an *ozonide*, $\begin{array}{l} NO_2\cdot C_6H_3\cdot CH \\ \;\;\;\;\;\;\;\;\;\;\;\;|\;\;\;\;\;\;\;\;|\!>\!O_3 \\ \;\;\;\;\;\;\;\;\;\;CO—CPh \end{array}$, whilst for the compound of m. p. 136° the formula $\begin{array}{l} NO_2\cdot C_6H_3\cdot CH \\ \;|\!>\!O_3 \\ \;\;\;\;\;CO_2H\cdot CPh \end{array}$ is suggested. Analyses were made in both cases.

The transformation product (of m. p. 320°) of 4-nitro-2-phenylindone was unaffected by ozone under the conditions of experiment.

R. V. S.

Explosiveness of the Residues from Ethereal Solutions of Nitrophenylindones Exposed to Light. III. MARUSSIA BAKUNIN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 375—378. Compare Bakunin and Lanis, Abstr., 1911, i, 992).—Ethereal solutions of nitrophenylindones which have been exposed to light yield on distillation an explosive residue. Ether and ethereal solutions of cinnamic acid did not yield an explosive residue after exposure to light in the same circumstances; if the explosive properties are due to ethyl peroxide, therefore, it is possible that the dissolved nitro-derivative favours its formation.

R. V. S.

Molecular Compounds of Aromatic Amines with Nitro-derivatives. DEMETRIUS E. TSAKALOTOS (*Bull. Soc. chim.*, 1912, [iv], 11, 284—288. Compare Abstr., 1908, i, 498).—Mixtures of aromatic amines with nitro-derivatives are intensely coloured, and Ostromisslensky (Abstr., 1911, ii, 195) has obtained spectroscopic evidence of

the formation of a definite molecular compound between aniline and nitrobenzene, although Kremann (Abstr., 1905, ii, 77) had shown that the fusion curve for mixtures of these two substances did not indicate the formation of such a compound. The author's previous work (*loc. cit.*) has shown that such compounds may only exist in the liquid state, and he has therefore examined viscosity and density curves for mixtures of (1) aniline and nitrobenzene, (2) dimethylaniline and nitrobenzene, and the fusion curve for α-mononitronaphthalene and α-naphthylamine, and finds that in these cases there is no indication of the formation of molecular compounds, so that the latter must be almost entirely dissociated even in the liquid state. Kremann (*loc. cit.*), however, has shown that stable compounds of this kind are formed between the aromatic amines and di- and tri-nitro-compounds. T. A. H.

Preparation of Diarylamines. KNOLL & Co. (D.R.-P. 241853).—Diarylamines have previously been prepared by heating arylamine hydrochlorides with elimination of ammonium chloride; the condensation of the bases is now found to take place readily in the presence of iodine.

2:2′-Dinaphthylamine (m. p. 170·5°) was obtained in quantitative yield by heating β-naphthylamine in the presence of 0·5% of iodine during four hours at 230°; in the absence of iodine a 10% yield only was obtained; this reaction also takes place in boiling aniline solution.

The following compounds were also prepared in the presence of iodine: 4:4′-Dihydroxydiphenylamine, m. p. 169°, in 70% yield at 200° from *p*-aminophenol; the triacetyl derivative has m. p. 132·5° (the previously recorded m. p.'s are 174·5° and 128·5° respectively).

α-Phenylnaphthylamine, m. p. 60°, b. p. 223°/10 mm., in 85% yield from aniline, and α-naphthylamine at 230—250° during eight hours.

α-o-*Methoxyphenylnaphthylamine*, m. p. 99·5°, b. p. 226—228°/11 mm.; the p-*methoxy*-compound has b. p. 250—252°/13 mm. α-o-*Tolylnaphthylamine* has b. p. 198—202°/9 mm.; the m-*tolyl* derivative, b. p. 234—237°/11 mm.; the p-*tolyl* derivative, m. p. 78°, b. p. 230°/10 mm.; the m-*xylyl* derivative, b. p. 227—232°/9 mm.; the p-*chlorophenyl* derivative, m. p. 102—103°, and the m-*chlorophenyl* derivative, m. p. 72·5°, b. p. 238—241°/12 mm.

β-*Phenylnaphthylamine* has m. p. 108°, b. p. 237°/15 mm.; the p-*chlorophenyl* derivative, m. p. 101°, b. p. 251·5°/13 mm., being obtained in 90% yield from β-naphthol and *p*-chloroaniline.

β-*m*-Tolylnaphthylamine has m. p. 68—69°, b. p. 243—246°/15 mm., yield 90% (previously recorded, m. p. 67°); the o-*tolyl* derivative, m. p. 95°, b. p. 235—237°/14 mm.; the o-*chlorophenyl* derivative, m. p. 89°, b. p. 236—238°/13·5 mm.; the m-*chlorophenyl* derivative, m. p. 101°, b. p. 250—253°/11 mm., and the p-*chloro*-o-*tolyl* derivative, m. p. 75°, b. p. 262—264°/15·5 mm.

Di-2 *naphthyl*-m-*phenylenediamine*, m. p. 234°, from β-naphthol and *m*-phenylenediamine at 200—260°, is obtained in quantitative yield. F. M. G. M.

The Action of Iodine on Phenols. II. The Catalytic Decomposition of Tri-iodophenol. JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1912, 31, 208—210. Compare Abstr., 1911, ii, 546).—The author has found that the addition of one drop of $N/10$-solution of iodine to a saturated solution of sodium tri-iodophenol produces a striking colour effect, the solution finally becoming semi-solid owing to the precipitation of tetraiododiphenylenequinone (compare Abstr., 1911, ii, 546). Investigation of this reaction has shown that (1) the reaction is truly catalytic, since no iodine is lost, the iodine in the final phase corresponding exactly with that added initially; (2) the acid liberated in the reaction is hydriodic acid, and (3) the weight of the tetraiododiphenylenequinone produced corresponds with that of the tri-iodophenol taken.

The reaction has a high initial velocity, and, in some cases, is practically complete in one hour. It does not proceed in neutral solution, the presence of a small quantity of free alkali being necessary. Excess of alkali, however, completely inhibits the reaction, it being difficult to obtain a satisfactory conversion if the alkali exceeds two mols. of sodium hydroxide per mol. of tri-iodophenol, and under such conditions the iodine is not recoverable. With solutions containing inhibitive amounts of alkali, reaction occurs if dilute acid is added cautiously to restore the optimum condition; carbon dioxide acts similarly if slowly bubbled through the solution. The addition of considerable amounts of iodine will also overcome the inhibitory effects of alkali.

The author considers that hypoiodous acid is the real catalyst, acting in accordance with the equations: $2I_2 + 2H_2O \rightleftarrows 2HI + 2HOI$; $2C_6H_2I_3ONa + 2HOI = C_{12}H_4I_4O_2 + 2I_2 + 2NaOH$. T. S. P.

Nitro-derivatives of Diphenyl Ether. ALPHONSE MAILHE and MARCEL MURAT (*Compt. rend.*, 1912, 154, 715—716).—When diphenyl ether is treated with fuming nitric acid in acetic acid solution at 50°, o- and p-*nitrodiphenyl ether*, $C_6H_5{\cdot}O{\cdot}C_6H_4{\cdot}NO_2$, are formed. The former is an oil, b. p. 185°/55 mm., whilst the latter crystallises in clinorhombic prisms, m. p. 56°; on reduction, it yields p-*aminodiphenyl ether*, $C_{12}H_{11}ON$, m. p. 82°. This amine develops an intense and persistent red coloration with bleaching powder.

A mixture is obtained when diphenyl ether is added to cold fuming nitric acid. Extraction of the product with boiling alcohol yields 2 : 4 : 2′ : 4′-tetranitrodiphenyl ether, $C_6H_3(NO_2)_2{\cdot}O{\cdot}C_6H_3(NO_2)_2$, m. p. 95°, and a more soluble *trinitro*-derivative, m. p. 108—110°. A second extraction yields a *pentanitro*-derivative, m. p. 86—88°. Extraction with carbon tetrachloride gives an ill-defined mixture, m. p. 110—120°, but subsequent treatment of the residue with ether removes the 4 : 4′-dinitro-derivative, m. p. 138—139°, and a very soluble 2 : 4 : 6 : 2′ : 4′ : 6′-*hexanitro*-derivative, m. p. 67°. If the original mixture of nitro-compounds is treated with sulphuric and nitric acids, an *octanitro*-derivative, m. p. 195°, is formed. The orientation of the compounds mentioned has not been definitely established

W. O. W.

m-Methylaminophenol. JOACHIM BIEHRINGER and A. TANZEN (*Chem. Zeit.*, 1912, **36**, 389).—m-Methylaminophenol can be satisfactorily prepared by methylating m-aminophenol with methyl iodide in the presence of potassium hydroxide solution at 100° in a sealed tube. It was obtained as a viscous oil, b. p. 169·5°/12 mm. (compare Gnehm and Scheutz, Abstr., 1901, i, 519); the *dibenzoyl* derivative,

$$NMeBz\cdot C_6H_4\cdot OBz,$$

forms colourless needles, m. p. 150°. D. F. T.

New Derivatives of Phenyl Sulphide. EDOUARD BOURGEOIS and P. HUBER (*Rec. trav. chim.*, 1912, **31**, 30—32).—o- and p-Aminophenyl sulphides are obtained by reduction of the corresponding nitro-compounds with tin and hydrochloric acid. The o-*aminophenyl sulphide*, $NH_2\cdot C_6H_4\cdot SPh$, crystallises from alcohol in colourless, transparent tablets, m. p. 35·5°, b. p. 212°/25 mm., 257·5°/100 mm. The para-compound crystallises in white needles, m. 96° (Kehrmann and Bauer, Abstr., 1897, i, 27, give 93°). These two bases on diazotisation and boiling with water give the corresponding hydroxy-compounds. o-*Hydroxyphenyl sulphide*, $SPh\cdot C_6H_4\cdot OH$, is a viscous, yellow liquid, b. p. 219°/66 mm., and the para-*compound* a white solid, m. p. 25°. W. G.

Trinitroanisoles. H. VERMEULEN (*Rec. trav. chim.*, 1912, **31**, 101—104. Compare Abstr., 1906, i, 256; and Blanksma, Abstr., 1904, i, 577; 1908, i, 979).—The trinitroanisoles were all obtained from the dinitroanisoles, using for nitration a mixture of nitric acid (D 1·5) and sulphuric acid in equal volumes.

2:3-Dinitroanisole yields 2:3:4-trinitroanisole, m. p. 155° (compare Meldola and Eyre, Trans., 1902, **81**, 993), which when acted on by sodium methoxide gives 2:4-dinitro-1:3-dimethoxybenzene. 3:6-Dinitroanisole is converted into 3:4:6-*trinitroanisole*, m. p. 106—107°, which gives 4:6-dinitro-1:3-dimethoxybenzene with sodium methoxide, thus orientating the third nitro-group. 3:4-Dinitroanisole yields a mixture of 2:3:4- and 3:4:6-trinitroanisoles. 3:5-Dinitroanisole on nitration gives 2:3:5-trinitroanisole, m. p. 104°, and a small quantity of 3:4:5-*trinitroanisole*, m. p. 119—120°. With sodium methoxide, the former yields 3:5-dinitroveratrole, and the latter, 4:5-dinitro-1:3-dimethoxybenzene. W. G.

α-p-Methoxyphenylethylamine [α-Anisylethylamine]. MARIO BETTI and GIUSEPPE DEL RIO (*Gazzetta*, 1912, **42**, i, 283—288).—The authors have resolved the base into the optical isomerides by crystallisation of the hydrogen tartrates from alcohol. The less soluble *hydrogen tartrate*, $C_9H_{13}ON(C_4H_6O_6)$, forms large, lustrous crystals. It has α^{20} $+1·66°$ in 5% aqueous solution (200 mm. tube). The free base liberated from it has $[\alpha]_D^{23}$ $+22·68°$ in light petroleum (concentration 3·704%). Its *benzoyl* derivative crystallises in long needles, m. p. 129°, and has α $+0·80°$ in 1% alcoholic solution and in 400 mm. tube at about 20°. The more soluble *hydrogen tartrate*,

$$C_9H_{13}ON(C_4H_6O_6),$$

has α $+1·12$—$1·16°$ in 5% aqueous solution in a 200 mm. tube at about

20°. The free base has $[\alpha]_D$ $-19\cdot13°$. Its *benzoyl* derivative has m. p. 138°, and α $-0\cdot74°$ in 1% alcoholic solution in a 400 mm. tube at about 20°. R. V. S.

Haloid Derivatives of Ditolyl Ethers. ALPHONSE MAILHE and MARCEL MURAT (*Bull. Soc. chim.*, 1912, [iv], **11**, 288—294).—A more detailed account of work published already (this vol., i, 254), in the course of which some further compounds are described. The mono-halogenated substances have the halogen atom in the para-position with respect to the ether linking, and the di-halogenated compounds have a halogen atom in the para-position in each of the two rings, except in the di-*p*-tolyl ethers, where the ortho-positions are occupied by the halogen atoms.

Chlorodi-*o*-tolyl ether has D^{10} 1·1741, n_D 1·590. Dichlorodi-*o*-tolyl ether has D^{9} 1·2980, n_D 1·611. *Bromo-di-o-tolyl ether*, b. p. 323—325°, D^{9} 1·4090, n_D 1·613, is a viscous liquid. The *dibromo*-derivative boils at 250°/15 mm.

Chlorodi-m-*tolyl ether*, b. p. 312°, D^{13} 1·1630, n_D 1·588, and the corresponding *dichloro*-compound, b. p. 336—338°, D^{18} 1·2882, n_D 1·606, are both very viscous liquids. Bromodi-*m*-tolyl ether, b. p. 330°/755 mm., n_D 1·624, is liquid, whilst the dibromo-compound, already described by Cook (Abstr., 1910, i, 731), is solid, m. p. 120°.

Chlorodi-*p*-tolyl ether, D^{10} 1·18, n_D 1·602, and the dichloro-derivative are both liquid. Bromo-di-*p*-tolyl ether has n_D 1·620. T. A. H.

4-Amino-α-naphthyl Mercaptan. II. THEODOR ZINCKE and FRANZ SCHÜTZ (*Ber.*, 1912, **45**, 636—645. Compare this vol., i, 257).—4-Amino-α-naphthyl methyl sulphide in alcoholic solution reacts with amyl nitrite and concentrated hydrochloric acid to form 1-*methylthiolnaphthalene-4-diazonium chloride*, $SMe\cdot C_{10}H_6\cdot N_2Cl$, decomp. 120°, green needles or leaflets. The diazo-compound is stable, forms a *platinichloride, chromate, nitrate, sulphate, bromide*, and *perbromide*,

$$C_{11}H_9N_2SBr_3,$$

decomp. 135°, and condenses normally with β-naphthol and with dimethylaniline to form respectively 1-*methylthiolnaphthalene-4-azo-β-naphthol*, $SMe\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_6\cdot OH$, green crystals with red fracture, and 1-*methylthiolnaphthalene-4-azodimethylaminobenzene*,

$$SMe\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot NMe_2,$$

m. p. 155°, purple-red leaflets (*hydrochloride*, green powder). The diazo-compound is reconverted into 4-amino-α-naphthyl methyl sulphide by stannous chloride or sulphurous acid, but is changed by cold 10% potassium sulphite to 1 : 1′-*dimethylthiol*-4 : 4′-*azonaphthalene*, $N_2(C_{10}H_6\cdot SMe)_2$, dark red prisms with a green lustre, and by a mixture of 40% potassium hydrogen sulphite and cold saturated aqueous potassium chloride to *potassium* 1-*methylthiolnaphthalene-4-diazosulphonate*, $SMe\cdot C_{10}H_6\cdot N_2\cdot SO_3K$, m. p. about 220° (decomp.), yellow leaflets. The *sodium* salt, decomp. 200°, and the *barium* and the *silver* salts of the latter are described. The diazosulphonate is converted into the diazonium chloride by concentrated hydrochloric acid, and reacts in boiling water with zinc dust and acetic acid to form, after the addition of hot saturated potassium chloride, *potassium* 1-*methylthiol*-

naphthalene-4-hydrazinesulphonate, $SMe\cdot C_{10}H_6\cdot NH\cdot NH\cdot SO_3K$, decomp. 199—200°, colourless needles, which is decomposed by hydrochloric acid, yielding nitrogen, ammonia, sulphuric and sulphurous acids, and 4-amino-α-naphthyl methyl sulphide. The impure *hydrazine* has been obtained as an oil from the *barium hydrazinesulphonate*; by acetylation it yields the *acetyl* derivative, $SMe\cdot C_{10}H_6\cdot NH\cdot NHAc$, m. p. 216°, glistening leaflets.

4-Dimethylamino-α-naphthyl methyl sulphide reacts with amyl nitrite and formic acid (D 1·2) to form 4-*methylthiol-β-naphthaquinone*, $SMe\cdot C_{10}H_5O_2$, m. p. 197°, brownish-red needles, which is reduced to a colourless, unstable *quinol*, yields β-naphthaquinoneanilide or dianilide by treatment with aniline under suitable conditions, dichloro-β-naphthaquinone by treatment with chlorine, 2-hydroxy-α-naphthaquinone by treatment with alkalis, and reacts with *o*-phenylenediamine to form the *naphthaphenazine*, $SMe\cdot C_{10}H_5<\substack{N\\N}>C_6H_4$, m. p. 170°, yellow needles.

C. S.

Phenol–Quinone Isomerism of the Schiff's Bases of Aromatic Hydroxyaldehydes. WILHELM MANCHOT and BERTIL PALMBERG (*Annalen*, 1912, 388, 103—135).—The mutually interchangeable "yellow" and "red" modifications of *p*-homosalicylideneaniline and of ethyl salicylidene-*p*-aminobenzoate have been already described (Abstr., 1909, i, 805; 1910, i, 33; 1911, i, 36). Two new examples are now given. *α-2-Hydroxynaphthylidene*-p-*aminophenol*, $OH\cdot C_{10}H_6\cdot CH{:}N\cdot C_6H_4\cdot OH$, when prepared by the rapid cooling of a concentrated alcoholic solution of its components, is obtained in yellow needles, m. p. 222°. When prepared by slow crystallisation or by keeping the yellow needles in contact with their mother liquor, the substance is obtained in the "red" modification, orange-yellow prisms, m. p. 226°; this form is converted into the "yellow" modification by rapid crystallisation from alcohol. In a similar manner, *ethyl* p-*homosalicylidene*-p-*aminobenzoate*,

$$OH\cdot C_6H_3Me\cdot CH{:}N\cdot C_6H_4\cdot CO_2Et,$$

has been obtained in a "yellow" modification (individual crystals appear as almost colourless, six-sided plates under the microscope) and a "red" modification, m. p. 101° (individual crystals appear as yellow or orange-red prisms); the "yellow" form becomes red at about 80°, melts at 90°, resolidifies, and melts again at 101°.

The isomerism in each of the preceding four cases is somehow connected with the hydroxyl group in the aldehyde, because only one compound is obtained in each case when the methyl or ethyl ether of the hydroxyaldehyde is condensed with the amine. It is suggested that the "yellow" and the "red" modifications may be represented by the respective formulæ, $NR{:}CH\cdot C_6H_4\cdot OH$ and

$$NR{:}CH\cdot C<\substack{CO\cdot CH_2\\CH-CH}>CH;$$

the "yellow" modification reacts more rapidly with cold alcoholic ferric chloride. Attempts have been made to prepare, from the "yellow" and the "red" modifications of an anil, derivatives corresponding with each of these formulæ, but they have been unsuccessful

on account of the ease with which the "yellow" and the "red" modifications change into one another; only in the case of ethyl *p*-homosalicylidene-*p*-aminobenzoate has the "yellow" modification been converted into a *hydrobromide*, $C_{17}H_{17}O_3N,HBr$, m. p. 207°, and the "red" modification into a *hydrobromide*, m. p. 215—216°.

The following compounds, each of which occurs in only one modification, are described: *α-2-Hydroxynaphthylideneaniline*,

$$OH\cdot C_{10}H_6\cdot CH\colon NPh,$$

m. p. 92°, almost colourless, six-sided leaflets; by crystallisation from aqueous alcohol, the substance is obtained in hydrated, yellow needles, m. p. 90—100°, but the red leaflets described by Knoevenagel and Schröter are shown to be a mixture of the anil and a red oxidation product, m. p. 265°, the composition of which could not be settled definitely by analysis. *α-2-Ethoxynaphthylidene-*p*-aminophenol*,

$$OEt\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_4\cdot OH,$$

m. p. 188°, almost colourless prisms; *α-2-hydroxynaphthylidene-*p*-anisidine*, $OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_4\cdot OMe$, yellow needles, m. p. 108°; *ethyl α-2-hydroxynaphthylidene-*p*-aminobenzoate*,

$$OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_6H_4\cdot CO_2Et,$$

m. p. 140°, slender needles, and its *ethyl ether*, m. p. 103·5°, colourless crystals; *α-2-hydroxynaphthylidene-α-naphthylamine*, m. p. 178°, orange-red crystals; *α-2-hydroxynaphthylidene-β-naphthylamine*, m. p. 140°, orange-yellow needles; *methyl* p-*homosalicylidene*-p-*aminobenzoate*, $OH\cdot C_6H_3Me\cdot CH\colon N\cdot C_6H_4\cdot CO_2Me$, m. p. 162°; p-*homosalicylidene*-p-*aminobenzoic acid*, m. p. 265°; p-*homosalicylidene*-p-*aminophenol*, m. p. 171°, orange-red crystals; p-*homosalicylidene*-p-*anisidine*, m. p. 122°; 2-*methoxy*-5-*methylbenzylidene*-p-*aminophenol*, m. p. 190·5°, colourless crystals; 2-*methoxy*-5-*methylbenzylidene*-p-*anisidine*, m. p. 90°, colourless needles; *salicylideneanthranilic acid*,

$$OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_4\cdot CO_2H,$$

has been obtained as a light yellow, crystalline mass, m. p. 196—197°, and as red crystals, m. p. 202—203°, but the evidence is not conclusive that these are "yellow" and "red" modifications respectively; *salicylidene*-p-*aminophenol*, m. p. 140°, yellow plates; *salicylidene*-p-*anisidine*, m. p. 84°, colourless, hexagonal leaflets; o-*methoxybenzylidene*-p-*aminophenol*, m. p. 168°, colourless leaflets. C. S.

The Action of Polyhydric Phenols on Uranium Salts. J. A. Siemssen (*Chem. Zeit.*, 1912, 36, 353—354).—The addition of resorcinol, quinol, catechol, pyrogallol, phloroglucinol, etc., to the yellow solutions of uranium salts gives intensely red solutions, the tone of which varies from a light red to a purple-red, according to the concentration (compare Weinland and Binder, *ibid.*, 208). Experiments in which resorcinol was chiefly used showed that cotton is not dyed by such solutions, even in the presence of potassium hydrogen sulphate. Wool is dyed yellow, the colour becoming more intense on treatment with ammonia, and being very resistant towards cold alkalis and acids and towards warm soap and soda solutions; it is also completely fast to light. The compound to which the colour is due has not been isolated. T. S. P.

Triphenylcarbinols. III. HUGO KAUFFMANN and PAUL PANNWITZ (*Ber.*, 1912, **45**, 766—776).—Certain triphenylcarbinols containing methoxy-groups can be reduced to the corresponding triphenylmethane derivatives by alcoholic hydrogen chloride (Abstr., 1905, i, 773; 1909, i, 99). However, the acetaldehyde which is also produced frequently reacts with the product to form tarry substances. The reduction of the carbinol is effected far more conveniently by boiling formic acid. It is found that under conditions in which triphenylcarbinol itself is extremely slowly reduced, (i) the presence of a methoxyl group in the ortho-position to the methane carbon atom greatly facilitates the reduction; in the meta-position it has very little influence; in the para-position it has a slight facilitating influence. Several methoxy-groups in para-positions render the reduction more easy; (ii) the influence of hydroxyl groups is similar to that of methoxyl groups; (iii) halogen atoms in the benzene nuclei do not markedly affect the reducibility; (iv) chloroanil, malachite-green, rosolic acid, fluorescein, and triphenylmethane-dyes, such as magenta, are reduced extremely slightly or not at all; (v) the reducibility does not run pari passu with the basicity of the triphenylcarbinols.

The following new compounds are described: m-*Methoxytriphenylmethane*, leaflets, m. p. 86°. op′-*Dimethoxytriphenylcarbinol*, m. p. 115°, is prepared from *p*-methoxybenzophenone and magnesium *o*-anisyl iodide, and yields op′-*dimethoxytriphenylmethane*, m. p. 94°, by reduction, best by zinc dust and acetic acid. oo′p′-*Trimethoxytriphenylcarbinol*, m. p. 119°, prepared from magnesium *o*-anisyl iodide and 2 : 4-dimethoxybenzophenone, is easily reduced to oo′p′-*trimethoxytriphenylmethane*, m. p. 118°. 5-*Bromo*-2 : 4-*dimethoxytriphenylcarbinol*, m. p. 186°, is obtained by the bromination of 2 : 4-dimethoxytriphenylcarbinol in carbon disulphide or concentrated sulphuric acid, and yields 5-*bromo*-2 : 4-*dimethoxytriphenylmethane*, m. p. 176°, by reduction. 5-*Chloro*-2 : 4-*dimethoxytriphenylcarbinol*, m. p. 182°, obtained by treating 2 : 4-dimethoxytriphenylcarbinol in chloroform with phosphorus pentachloride and subsequently with water, is reduced, as easily as the preceding bromo-compound, to 5-*chloro*-2 : 4-*dimethoxytriphenylmethane*, m. p. 159.

Michael's salicylresorcinol is shown to be resorcinyl salicylate, not 2 : 2′-4′-trihydroxybenzophenone as has hitherto been supposed.

C. S.

Action of Magnesium Phenyl Bromide on Methylpinacolin. (Mme.) PAULINE RAMART-LUCAS (*Compt. rend.*, 1912, **154**, 708—710). —The tertiary alcohols obtained by applying the Grignard reaction to trialkylacetophenones (Abstr., 1910, i, 378) undergo dehydration when heated with acetyl chloride and acetic anhydride, giving the corresponding hydrocarbons. The constitution of γ-phenyl-$\beta\beta$-dimethylbutan-γ-ol (*loc. cit.*) and of the corresponding pentanol has been completely established by their synthesis from pinacolin and methylpinacolin respectively by the action of magnesium phenyl bromide. The occurrence of acetophenone amongst the products formed by the action of chromic acid on γ-phenyl-$\beta\beta$-dimethylbutan-γ-ol is probably due to the intermediate formation of a hydrocarbon containing the

trimethylene ring, arising through a dehydrating action of the oxidising mixture. W. O. W.

Dipterocarpol. LEOPOLD VAN ITALLIE (*Pharm. Weekblad*, 1912, **49**, 314—321).—*Dipterocarpol* is a phytosterol isolated from the balsam of *Dipterocarpus Hasseltii* and *D. trinervis* by extracting with boiling alcohol the part insoluble in light petroleum. It forms colourless plates, m. p. 134—135°, $[\alpha]_D + 64 \cdot 6°$, molecular formula $C_{27}H_{46}O_2$. It answers the phytosterol tests of Liebermann, Hesse, Mach, Hirschsohn, and Tschugaeff.

When heated at 160° under pressure with anhydrous sodium acetate and acetic anhydride, it yields, by elimination of H_2O, *dipterocarpol anhydride*, $C_{27}H_{44}O$, colourless, doubly refracting crystals, m. p. 69—70°, which answers to the same tests as the parent substance. Phenylcarbimide also reacts, forming the anhydride, but no product was obtained with either benzoyl chloride or benzoic anhydride.

Oxidation with Kiliani's chromic acid mixture converts the phytosterol into the corresponding ketone, *dipterocarpone*, $C_{27}H_{44}O_2$, colourless, columnar, rhombic crystals, m. p. 183—184°, $[\alpha]_D + 71 \cdot 03°$, which answers the phytosterol tests. Its formation indicates the presence of a CH·OH-group in dipterocarpol. *Dipterocarpoxime*, $C_{27}H_{44}O_2$:NOH, forms microscopic, colourless crystals, m. p. 249—250°.

With halogens, dipterocarpol forms additive products, which could not be obtained crystalline. Reduction with sodium and amyl alcohol did not yield any crystalline product. A. J. W.

Olivil. WILHELM KOERNER and BARTOLO L. VANZETTI (*Mem. R. Accad. Lincei*, 1911, [v], 8, 749—792. Compare Abstr., 1903, i, 430). —The authors give a full account of the work on this subject previously reported (*loc. cit.*), and some new derivatives are described. Olivil ethyl alcoholate has m. p. about 120°, and $[\alpha]_D^{22} - 23 \cdot 8°$ (in ethyl alcohol). Olivil hydrate has m. p. about 105°, and $[\alpha]_D^{12} - 127°$ (in water). Olivil methyl alcoholate has m. p. about 97°, and $[\alpha]_D^{22} - 48 \cdot 9°$ (in methyl alcohol). Olivil propyl alcoholate has m. p. about 104°. Olivil *iso*propyl alcoholate has m. p. 101·5°. Olivil allyl alcoholate has m. p. 99·5—106°.

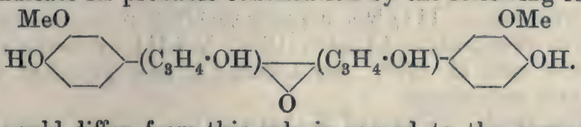
Dimethylolivil, $C_{18}H_{16}O_3(OMe)_4$, crystallises in small, silky needles, m. p. 156°, $[\alpha]_D^{24} - 56 \cdot 4°$ (in alcohol). When treated with bromine in glacial acetic acid solution, dimethylolivil yields a *monobromo*-derivative, $C_{22}H_{27}O_7Br$, which crystallises in colourless scales, m. p. 128°, and also a *dibromo*-derivative, $C_{22}H_{26}O_7Br_2$, which forms (with 1 mol. of benzene) silky needles, m. p. about 85°, or (anhydrous) spherical aggregates of needles, m. p. 132°. Dimethylolivil also yields a derivative with *mercuric acetate*, $C_{22}H_{26}O_6(HgAc)_2$, and with *mercuric chloride*, $C_{22}H_{26}O_6(HgCl)_2$. *Monomethylolivil*, $C_{21}H_{26}O_7$. is obtained when olivil is treated with about three-fourths of the amount of methyl iodide calculated for complete methylation; it crystallises in woolly needles, m. p. 218° (if the bath is previously heated to 200°). *Diethylolivil*, $C_{24}H_{32}O_7$, crystallises in needles, m. p. 182°. *Monoethylolivil*, $C_{22}H_{28}O_7$, has m. p. 145°. *Methylethylolivil*, $C_{23}H_{30}O_7$, can be prepared either from monoethylolivil or from monomethylolivil; it crystallises in needles. m. p. about 169° *Dipropylolivil*, $C_{26}H_{36}O_7$,

forms long, thin needles, m. p. 135·5° *Dibenzylolivil*, $C_{34}H_{36}O_7$, crystallises in silky needles, m. p. 150—157°, according to the mode of heating.

*iso*Olivil, $C_{18}H_{16}O_3(OH)_2(OMe)_2$, forms prismatic crystals, m. p. 167°; it has $[\alpha]_D^{12}$ +352° (in water), $[\alpha]_D^{12}$ +118° (in acetic acid), $[\alpha]_D^{25}$ +61·1° (in alcohol). With concentrated sulphuric acid it gives a deep orange-red coloration, which becomes violet on addition of water, and with ferric chloride it yields a fugitive blue coloration, which becomes green and finally brown. With ethyl alcohol, *iso*olivil yields an *alcoholate*, $C_{20}H_{24}O_7,\frac{1}{2}EtOH$, which forms tabular crystals. The *methyl alcoholate*, $C_{20}H_{24}O_7,2MeOH$, crystallises in tablets. The *compound* with ethyl ether, $C_{20}H_{24}O_7,Et_2O$, and the *compound* with acetone, $C_{20}H_{24}O_7,COMe_2$, are also crystalline.

*Dimethyl*iso*olivil*, $C_{18}H_{16}O_3(OMe)_4$, crystallises in silky needles, m. p. 184·5°, $[\alpha]_D^{22·5}$ +33·58°. *Monomethyl*iso*olivil*, $C_{18}H_{16}O_3(OH)(OMe)_3$, forms prismatic crystals (with methyl alcohol) or thin needles (with $2H_2O$) [Repossi: the hydrate crystallises in the tetragonal system, $a:c=1:0·91654$]; the anhydrous substance has m. p. 208°. *Diethyl*iso*olivil*, $C_{24}H_{32}O_7$, crystallises in needles, m. p. 179—179·5°, $[\alpha]_D^{22·5}$ +38·22° (in alcohol). *Monoethyl*iso*olivil*, $C_{22}H_{28}O_7$, crystallises with $2H_2O$, and has m. p. 148—150° with subsequent partial solidification; the anhydrous substance is very hygroscopic. *Ethylmethyl*iso*olivil*, $C_{23}H_{30}O_7$ (prepared by ethylating monomethyl*iso*olivil), crystallises in groups of needles, m. p. about 189°, $[\alpha]_D^{25}$ +50·35° (in alcohol). *Methylethyl*iso*olivil*, $C_{23}H_{30}O_7$ (prepared by methylating monoethyl*iso*olivil), has m. p. 168°, $[\alpha]_D^{25}$ +46·3° (in alcohol). *Benzylmethyl*iso*olivil*, $C_{28}H_{32}O_7$ (from monomethyl*iso*olivil), crystallises in soapy needles, m. p. 173—174°.

In view of the reactions of olivil now and formerly described, the authors indicate its probable constitution by the following formula:



*iso*Olivil would differ from this only in regard to the arrangement of atoms in the side-chain. R. V. S.

Direct Hydrogenation of Alkyl Benzoates by Catalysis: Preparation of Alkyl *cyclo*Hexanecarboxylates. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1912, **154**, 922—925).—Benzoic acid and its esters, which are the aromatic compounds most easily hydrogenated by the ordinary method, have hitherto proved the most difficult to attack by the catalytic method in presence of reduced nickel. Very small quantities of *cyclo*hexanecarboxylic acid are formed when benzoic acid and a large excess of hydrogen are passed over nickel below 200°.

When methyl benzoate and hydrogen are passed over nickel at 210—225°, the metal rapidly loses all activity as a catalyst, owing to the formation of a film of nickel benzoate. By operating at 180°, however, with a large excess of hydrogen, the action proceeds readily in the normal way. From ethyl benzoate at 180°, a good yield of

ethyl *cyclo*hexanecarboxylate, D^{16} 0·962, n_D^{16} 1·452, is obtained. *iso*-Amyl benzoate gave an 80% yield of iso*amyl* cyclo*hexanecarboxylate*, b. p. 247°, D^{13} 0·934, n_D^{13} 1·458. W. O. W.

[Preparation of 2 : 4-Dichlorophenylthiolacetic Acid.] KALLE & Co. (D.R.-P. 241839).—2 : 4-*Dichlorophenylthiolacetic acid*, colourless needles, is prepared from 2 : 4-dichloroaniline by successive diazotisation, xanthogenation, followed by treatment with sodium hydroxide and chloroacetic acid; after treatment with concentrated sulphuric acid, it yields a vat dye (violet powder), which dyes cotton a fast violet-red. F. M. G. M

[Preparation of ψ-Cumylthiolacetic Acid.] KALLE & Co. (D.R.-P. 241910).—*ψ-Cumylthiolacetic acid*, colourless needles, is prepared by known methods from 5-chloro-*o*-toluidine. The patent contains a tabulated summary of the properties of numerous vat dyes prepared from arylthiolacetic acid obtained from toluidines, xylidines, ψ-cumidines, anisidines, phenetidines, naphthylamines, and their halogen and nitrated derivatives. F. M. G. M.

Two Compounds Formed by Iodine and Tyrosine obtained by the Tryptic Hydrolysis of Proteins. PAUL MACQUAIRE (*Compt. rend.*, 1912, **154**, 938—939).—Analyses confirm the identity of di-iodotyrosine from peptone (this vol., i, 58) and that prepared by the action of iodine on tyrosine. On prolonged boiling of di-iodotyrosine with water, a portion of the iodine is eliminated, and a more stable, coloured, amorphous substance formed. W. O. W.

Further Study of Two of the Products of the Transformation of *p*-Sulphamidobenzoic Acid when Heated to 220°. JOSEPH S. CHAMBERLAIN (*Amer. Chem. J.*, 1912, **47**, 318—333).—Stoddard (this vol., i, 111) has investigated the products obtained by Remsen and Muckenfuss (Abstr., 1896, i, 481) by heating *p*-sulphamidobenzoic acid at 220°. An account is now given of a further study of these substances.

When the product obtained by heating the acid at 220° for eight hours is extracted with hot alcohol, the *ammonium* salt of *p*-benzoic sulphinide, $C_6H_4{<}{\substack{CO\\SO_2}}{>}N{\cdot}NH_4$, separates on cooling. The *barium* salt, $\left(C_6H_4{<}{\substack{CO\\SO_2}}{>}N\right)_2Ba,3H_2O$, *copper* salt, $\left(C_6H_4{<}{\substack{CO\\SO_2}}{>}N\right)_2Cu$, and *lead* salt, $\left(C_6H_4{<}{\substack{CO\\SO_2}}{>}N\right)_2Pb,3H_2O$, are also described.

By the action of magnesium hydroxide on the "infusible diamide," Stoddard (*loc. cit.*) obtained the magnesium salt,

$$\left[C_6H_4{<}{\substack{CO\\SO_2}}{>}\binom{NH_2}{O}\right]_2Mg.$$

On treating the diamide with barium hydroxide, however, the whole of the nitrogen is expelled as ammonia, and barium *p*-sulphobenzoate is produced, and an intermediate salt containing one atom of nitrogen cannot be obtained.

On heating a mixture of potassium hydrogen *p*-sulphobenzoate

and ammonium thiocyanate at 200°, a salt was obtained which was probably *potassium* p-*carbamidobenzenesulphonate*; the corresponding *sodium* salt was also prepared. E. G.

Study of the Products Formed by the Action of Heat on *p*-Sulphamido-*m*-toluic Acid. CAMPBELL E. WATERS (*Amer. Chem. J.*, 1912, **47**, 333—351).—In view of the results obtained on heating *p*-sulphamidobenzoic acid at 220° (Remsen and Muckenfuss, Abstr., 1896, i, 481; Stoddard, this vol., i, 111; Chamberlain, preceding abstract), a study has been made of the effect of heat on *p*-sulphamido-*m*-toluic acid.

Remsen and Iles have stated that this acid has m. p. 254·5—255°, but it is now found that the m. p. varies greatly with the rate of heating.

When the acid is heated for five to seven hours at 220°, it undergoes a similar change to that which takes place in the case of *p*-sulphamidobenzoic acid; the products of the change are *p*-sulpho-*m*-toluic acid, ammonium hydrogen *p*-sulphotoluate, and an infusible diamide of *p*-sulpho-*m*-toluic acid, but no evidence was obtained of the existence of an acid analogous to Remsen and Muckenfuss' *iso-p*-sulphamidobenzoic acid.

The *infusible diamide*, $C_6H_3Me{<}^{CO}_{SO_2}{>}(NH_2)_2$, crystallises in orthorhombic plates. Both nitrogen atoms are eliminated as ammonia by the action of sodium hydroxide or barium hydroxide, thus indicating that a sulphamido-group is not present. On boiling the compound with magnesium hydroxide, however, only one nitrogen atom is expelled, and the *magnesium* salt,

$$\left[C_6H_3Me{<}^{CO}_{SO_2}{>}\binom{NH_2}{O}\right]_2Mg,4H_2O,$$

of an acid isomeric with *p*-sulphamido-*m*-toluic acid is produced; the corresponding *barium* and *potassium* salts crystallise with $1H_2O$, the *zinc* salt with $5\frac{1}{2}H_2O$, and the *copper* salt with $3H_2O$; the *ammonium* salt forms rectangular prisms.

Barium p-*sulpho*-m-*toluate* crystallises in needles containing $2H_2O$; the *barium hydrogen* and *sodium hydrogen* salts crystallise with $5H_2O$ and $2\frac{1}{2}H_2O$ respectively. The *ammonium hydrogen* salt, prepared from the barium salt, or by the hydrolysis of *p*-sulphamido-*m*-toluic acid, was not identical with that obtained from the product of the prolonged fusion of the sulphamido-acid. E. G.

Preparation of Carboxylic Acids of Aromatic Ammonium Compounds or their Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 240835. Compare Abstr., 1911, i, 627; this vol., i, 176).—When ω-chloro-*p*-toluic acid, m. p. 195° (*loc. cit.* gives 190—192°), is heated at 60—70° during seven to eight hours with dimethylaniline, it yields the *compound*, $CO_2H\cdot C_6H_4\cdot CH_2\cdot NClMe_2Ph$, needles, m. p. 151° (decomp.). Similar products are formed when other tertiary bases are employed.

ω-*Chloro*-p-*toluonitrile*, colourless crystals, m. p. 78°, is prepared by chlorinating *p*-toluonitrile; when treated with pyridine it yields the *compound*, $C_5H_5NCl\cdot CH_2\cdot C_6H_4\cdot CN$, colourless needles readily soluble in alcohol or water. F. M. G. M.

Action of the Ultra-violet Rays on Stereoisomerides of the Cinnamic Series. II. MARUSSIA BAKUNIN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], **17**, 372—375. Compare Bakunin and Parlati, Abstr., 1907, i, 415; Bakunin and Lanis, Abstr., 1911, i, 992; Stoermer, *ibid.*, i, 295).—The most favourable results were obtained by keeping alcoholic solutions of the substances at a distance of a few centimetres from an uviol lamp for about 190 hours. The phenylcinnamic acid of m. p. 172° is unaffected. After twenty-four hours, the phenyl-*p*-nitrocinnamic acid of m. p. 143° is completely converted into that of m. p. 214°. The reverse change could not be effected. The phenyl-*m*-nitrocinnamic acid of m. p. 181° is converted slowly and partially into that of m. p. 195°, and the inverse change also occurs, but less readily. The phenyl-*o*-nitrocinnamic acid of m. p. 196° apparently yields traces of the isomeride of m. p. 147°.

4-Nitro-2-phenylindone and 6-nitro-2-phenylindone are very slightly affected by the ultra-violet rays. R. V. S.

Preparation of Hexamethylenetetramine Sulphosalicylates. J. D. RIEDEL (D.R.-P. 240612. Compare Abstr., 1893, i, 298; this vol., i, 168).—*Hexamethylenetetramine sulphosalicylate*

$$C_6H_{12}N_4,C_7H_6O_6S,$$

prismatic crystals, is prepared by treating an aqueous solution of hexamethylenetetramine (1 part) with an alcoholic solution of sulphosalicylic acid (2 parts); it is of therapeutic value, and is decomposed by hot dilute mineral acids with evolution of formaldehyde.

F. M. G. M

Some Derivatives of Benzoylpropionic Acid. (Attempted Synthesis of Hydroxyl Derivatives of Naphthalene.) GUIDO BARGELLINI and MICHELE GIUA (*Gazzetta*, 1912, **42**, i, 197—209).—The authors have attempted to obtain naphthalene derivatives: (1) by withdrawing H_2O from derivatives of benzoylpropionic acid, such as the lactone resulting from the reduction of anisoylpropionic acid with sodium amalgam; (2) by removing H_2O from benzoylpropionic acid, or MeOH from its methyl ester. In the present paper a number of methoxyl-derivatives of benzoylpropionic acid are described; they were obtained by condensing succinic anhydride with anisole and with other aromatic methoxy-compounds.

Anisoylpropionic acid, $OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, is obtained when anisole is treated with succinic anhydride in the presence of aluminium chloride, and is identical with that prepared by Poppenberg (Abstr., 1902, i, 60). On reduction with sodium amalgam it yields *anisyl-γ-butyrolactone*, which has m. p. about 45°. *Methyl anisoylpropionate*, $C_{12}H_{14}O_4$, forms white needles, m. p. 46—47°. 3 : 4-*Dimethoxybenzoylpropionic acid*, $C_{12}H_{14}O_5$ (from veratrole and succinic anhydride in the presence of aluminium chloride), crystallises in colourless needles, m. p. 160—161°. It gives a yellow coloration with concentrated sulphuric acid. 2 : 4-*Dimethoxybenzoylpropionic acid*, $C_{12}H_{14}O_5$ (from resorcinol dimethyl ether and succinic anhydride), has m. p. 146°. It gives a yellow coloration with concentrated sulphuric acid. 2 : 5-*Dimethoxybenzoylpropionic acid*, $C_{12}H_{14}O_5$ (from quinol dimethyl ether and succinic anhydride), forms

lustrous needles, m. p. 99—100°; it gives an orange-yellow coloration with concentrated sulphuric acid. 2 : 4 : 5-*Trimethoxybenzoylpropionic acid*, $C_{13}H_{16}O_6$ (from hydroxyquinol trimethyl ether and succinic anhydride), crystallises in colourless needles, m. p. 168—169°; it gives a yellowish-green coloration with concentrated sulphuric acid. Its *methyl* ester, $C_{14}H_{18}O_6$, forms colourless plates, m. p. 110—111°; it gives a pale yellow coloration with concentrated sulphuric acid.

When pyrogallol trimethyl ether is treated with succinic anhydride in the presence of aluminium chloride, 2-*hydroxy*-3 : 4-*dimethoxybenzoylpropionic acid*, $C_{12}H_{14}O_6$, is produced; it crystallises in colourless needles, m. p. 152°. With concentrated sulphuric acid the substance gives a yellow coloration, which becomes dark red on warming. With ferric chloride it gives a red coloration. It is not possible to esterify the free hydroxyl-group in this acid. *Methyl* 2-*hydroxy*-3 : 4-*dimethoxybenzoylpropionate*, $C_{13}H_{16}O_6$, forms colourless needles, m. p. 106°; it gives a yellowish-green coloration with concentrated sulphuric acid.

R. V. S.

Friedel-Crafts' Reaction. II. GUSTAV HELLER (*Ber.*, 1912, **45**, 665—673. Compare Abstr., 1908, i, 994).—To ascertain whether the complex, intermediate product, the existence of which is assumed in the formation of benzoylbenzoic acid (*loc. cit.*), can exert a condensing or catalytic action, phthalic anhydride, aluminium chloride, and benzene are allowed to react, the mass is cooled and treated with benzoyl chloride, and then is re-heated at 60—75°. The chief product is an additive *compound*, $C_{20}H_{18}O_2,AlCl_3$, of diphenylphthalide and aluminium chloride, the by-products, after the addition of water, being benzoic acid, benzophenone, and benzoylbenzoic acid. When ethyl bromide is used in place of the benzoyl chloride in the preceding experiment, no action occurs, and 99% of the theoretical yield of benzoylbenzoic acid is obtained.

When equal molecular quantities of phthalic anhydride, benzoyl chloride, benzene, and aluminium chloride are heated together, the reaction occurs preferentially with the phthalic anhydride rather than with the benzoyl chloride, 75·9% of the theoretical quantity of benzoylbenzoic acid being produced; the amount of benzophenone was not estimated.

[With ERICH GRÜNTHAL.]—Anthracylbenzoic acid (*loc. cit.*) has been obtained in stout prisms, m. p. 242—243°; it yields anthraquinone by treatment with chromic and acetic acids, showing that the phthaloyl group is attached to a *meso*-carbon atom.

α-Chloro-naphthalene, phthalic anhydride, and aluminium chloride react to form ultimately α-4-*chloronaphthoyl*-o-*benzoic acid*,

$$C_{10}H_6Cl\cdot CO\cdot C_6H_4\cdot CO_2H,$$

m. p. 172—174°, the constitution of which is proved by the formation of 1-hydroxy-4-naphthoic acid (following abstract) by fusion with potassium hydroxide at 250—255°. When heated with concentrated sulphuric acid at 60—70°, the acid yields 1-*chloro*-3 : 4-*naphthanthraquinone*, $C_6H_4{<}^{CO}_{CO}{>}C_{10}H_5Cl$, m. p. 180·5—181·5°, yellow needles. β-3-*Chloronaphthoyl*-o-*benzoic acid*, $C_{10}H_5Cl\cdot CO\cdot C_6H_4\cdot CO_2H$, m. p.

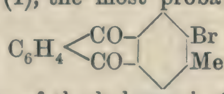
226—227°, prepared in a similar manner from β-chloronaphthalene, can be converted into 2-*chloro*-3 : 4-*naphthanthraquinone*, m. p. 233—234°, by sulphuric acid, and by oxidation by potassium permanganate yields a chlorinated acid by rupture of the naphthalene nucleus. C. S.

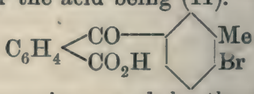
α-Naphthol-4-carboxylic Acid. GUSTAV HELLER [with HANS RUHTENBERG] (*Ber.*, 1912, **45**, 674—679).—*α-Naphthol*-4-*carboxylic acid*, $OH{\cdot}C_{10}H_6{\cdot}CO_2H$, m. p. 183—184°, is prepared by heating the corresponding aldehyde with potassium hydroxide and a little water at 250°. It crystallises in yellow needles, yields a chocolate precipitate with ferric chloride, and forms an *acetyl* derivative, m. p. 178—179°. It condenses with benzenediazonium chloride in alkaline solution to form benzeneazo-α-naphthol, yields nitroso-α-naphthol with nitrous acid, and by nitration in glacial acetic acid at 20° forms 2-*nitro*-*α-naphthol*-4-*carboxylic acid*, m. p. 258° (decomp.), yellow needles, which possesses dyeing properties and yields 2-*amino-α-naphthol*-4-*carboxylic acid*, m. p. 143° (decomp.), by reduction with alkaline sodium hyposulphite. The amino-acid gives a blood-red coloration with ferric chloride, and by treatment with 38% nitric acid (assisted by two drops of stronger acid) yields *β-naphthaquinone*-4-*carboxylic acid*, $C_{11}H_6O_4$, m. p. 164—165° (decomp.), yellowish-red crystals; the latter yields 1 : 2-*dihydroxy*-4-*naphthoic acid*, m. p. 195° (decomp.), by treatment with aqueous sodium hydrogen sulphite.

1-Hydroxy-4-naphthoic acid is converted by concentrated sulphuric acid at the ordinary temperature into 2-*sulpho-α-naphthol*-4-*carboxylic acid*, $C_{11}H_8O_6S$, m. p. 153° (decomp), the constitution of which is proved by the formation of benzeneazo-α-naphthol-2-sulphonic acid by condensation with benzenediazonium chloride. C. S.

Abnormal Friedel-Crafts' Reactions. GUSTAV HELLER [with ERICH GRÜNTHAL and HANS RUHTENBERG] (*Ber.*, 1912, **45**, 792—796).—*o*- and *p*-Chlorotoluenes combine with phthalic anhydride in presence of aluminium chloride to form the corresponding chlorotoluoylbenzoic acids (Abstr., 1908, i, 994).

The bromotoluenes behave differently: from *o*-, *p*-, or *m*-bromotoluene a mixture of several acids was obtained, from which only one bromotoluoylbenzoic acid could be isolated, which was in each case the same and yielded the same bromomethylanthraquinone having the formula (I), the most probable formula for the acid being (II). The

(I.) 

(II.) 

β-position of the halogen in the anthraquinone is proved by the fact that no condensation product was obtained on heating with aniline or *p*-toluidine and sodium acetate. When heated with sodium in amyl alcohol and zinc dust, 3-methylanthraquinone was formed.

p-*Bromo*-m-*toluoyl*-o-*benzoic acid* crystallises in long, colourless needles, m. p. 183—184°.

2-*Bromo*-3-*methylanthraquinone* separates in long, pale straw-yellow needles, m. p. 219—220°.

4-*Anilino*-1-*methylanthraquinone*, obtained from 4-chloro-1-methyl-

anthraquinone on heating with aniline and sodium acetate, crystallises in reddish-black, bent needles, m. p. 144°. The corresponding 4-*toluidino*-1-*methylanthraquinone* separates in deep red rods, m. p. 159—160°. 2-Anilino-1-methylanthraquinone does not react with aniline or toluidine. E. F. A.

Hydroxyphenyl-, Hydroxy-*p*-tolyl-, and Hydroxydiphenyl-homocampholic Acids and Their Transformation into Benzylidene-, *p*-Tolylidene-, and Diphenylmethylene-camphors. ALBIN HALLER (*Compt. rend.*, 1912, **154**, 742—748. Compare Abstr., 1900, i, 452).—Hydroxyphenylhomocampholic acid, produced by the hydrolysis of benzylidenecamphor with hydrogen bromide, separates from methyl or ethyl alcohol below 50° in efflorescent crystals containing a molecule of alcohol, which is only lost at 130°; the product then has m. p. 205—207°. Hydroxy-*p*-tolylhomocampholic acid has m. p. 164° (not 217° as stated previously), $[\alpha]_D$ +71·45°; the *sodium* salt is readily hydrolysed by water. *Hydroxydiphenylhomocampholic acid*, $OH\cdot CPh_2\cdot CH_2\cdot C_8H_{14}\cdot CO_2H$, occurs in leaflets, m. p. 210°, $[\alpha]_D$ +111·06°; the *sodium* salt crystallises in pearly leaflets very sparingly soluble in water.

When heated with excess of acetyl chloride the foregoing acids lose $2H_2O$, and form the parent unsaturated compounds. Benzylidenecamphor and its homologues regenerated in this way show no loss in rotatory power. In the last instance, a yellow *compound*, m. p. 123°, formed simultaneously in small quantities, appears to be isomeric with diphenylmethylenecamphor. W. O. W.

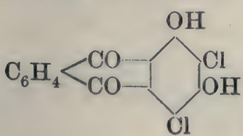
Dichlorodihydroxybenzoylbenzoic Acid: its Conversion into Tetrachlorofluorescein and into Anthraquinone Derivatives. CARL METTLER (*Ber.*, 1912, **45**, 800—804).—It is possible to chlorinate dihydroxybenzoylbenzoic acid by means of sulphuryl chloride with the formation of 3 : 5-dichloro-2 : 4-dihydroxybenzoylbenzoic acid, $C_6HCl_2(OH)_2\cdot CO\cdot C_6H_4\cdot CO_2H$, which when heated above the melting point is converted into tetrachlorofluorescein. This dyes silk in practically the same manner as eosin, the colour being perhaps a shade more yellow.

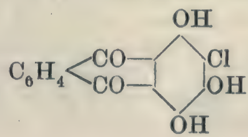
When dichlorodihydroxybenzoylbenzoic acid is condensed with fuming sulphuric acid and boric acid, dichloroxanthopurpurin or chloropurpurin are produced according to the temperature.

3 : 5-*Dichloro*-2 : 4-*dihydroxybenzoylbenzoic acid* crystallises in cubes, m. p. 222° (decomp.).

Tetrachlorofluorescein is a red, crystalline powder, which softens at 295°, m. p. 305°.

Dichloroxanthopurpurin (I) is a yellow, crystalline powder, m. p.

(I.) 

(II.) 

236—238°, the solution in sulphuric acid is yellow, and it dissolves in sodium carbonate with a reddish-orange coloration.

Chloropurpurin (II) crystallises in deep red needles, m. p. 270—273°. It dissolves in sodium carbonate with a brownish-red and in sulphuric acid with a purple-red coloration. E. F. A.

Chromoisomerides. ARNALDO PIUTTI and E. DE' CONNO (*Mem. R. Accad. Lincei*, 1911, [v], 8, 793—810).—The authors have investigated the absorption spectra of solutions of a number of the pairs of isomeric compounds formerly described (compare Piutti, Abstr., 1910, i, 672) with a view to determining in which cases the isomerism is physical, and in which chemical. The measurements were effected by Hartley's method, but the arc between iron electrodes (containing some manganese) was employed as the source of light. For each substance photographs were taken of the absorption spectra at ten different concentrations. The white and yellow forms of *p*-methoxyphenylphthalimide have the same absorption spectrum, and are therefore not chemical isomerides. [SCACCHI : the white isomeride crystallises in the rhombic system, $a : b : c = 1\cdot0096 : 1 : 1\cdot0464$.]

The two forms of *p*-methoxyphenylmaleinimide (m. p. 145—146° and 148·5° respectively) have different absorption spectra, and are therefore assigned the formulæ :

$$\begin{array}{l} HC—C{:}N\cdot C_6H_4\cdot OMe \\ \;\,\|\qquad >O \\ HC—C{:}O \end{array} \qquad \text{and} \qquad \begin{array}{l} HC—C{:}O \\ \;\,\|\qquad >N\cdot C_6H_4\cdot OMe \\ HC—C{:}O \end{array}$$

respectively. The two *p*-ethoxyphenylmaleinimides (m. p. 127° and 134—135° respectively) have also different absorption spectra, and are consequently assigned formulæ analogous to the above.

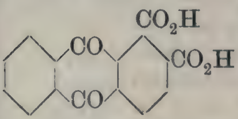
3-Nitroaceto-*p*-toluidide crystallises in two forms, which have the same absorption spectrum, and the same is true of the two forms of 2 : 4-dinitrophenyl-*o*-tolylamine.

p-Hydroxy-, *p*-methoxy-, and *p*-ethoxy-phenylpyrocinchonimides each exist in two forms (white and yellow) ; the absorption spectra of all six are identical, so that the pairs are physical isomerides. The different substituting groups make no perceptible difference to the absorption spectrum.

p-Hydroxyphenylitaconamic acid exists in three forms: (1) m. p. 161—162° (white) ; (2) m. p. 118—119° (yellow) ; (3) m. p. 97—98° (white). *p*-Methoxyphenylitaconamic acid exists in three forms : (1) m. p. 166—167° (white) ; (2) m. p. 144—145° (yellow) ; (3) m. p. 135—136° (white). *p*-Ethoxyphenylitaconamic acid also exists in three forms : (1) m. p. 165—166° ; (2) m. p. 148—149° ; (3) m. p. 134—135°. Of these nine isomerides, the three numbered (1) and the three numbered (3) have identical absorption spectra, whilst the remaining three numbered (2) have a different absorption spectrum (which is identical in all three cases).

The two forms of *p*-methoxy- and *p*-ethoxy-phenylfumardiamides show different absorption spectra, and therefore these pairs are not physical isomerides. R. V. S.

Preparation of Anthraquinone-1 : 2-dicarboxylic Acids. Roland Scholl (D.R.-P. 241624).—*Anthraquinone-1 : 2-dicarboxylic acid* (annexed formula), a yellow, crystalline meal, is readily prepared by oxidising naphthanthraquinone with either chromic acid, nitric acid, potassium permanganate, or potassium chlorate in the presence of sulphuric acid. The acid has m. p. 270° (approx.), at about which temperature it is converted into the *anhydride*, m. p. 322—324°, which can also be obtained by dissolving the acid in hot acetic anhydride. F. M. G. M.



2 : 6-Dinitrobenzaldehyde. Siegmund Reich [and J. Pinczewski] (*Ber.*, 1912, **45**, 804—809).—2 : 6-Dinitrobenzaldehyde has been prepared by the following series of reactions. 2 : 6-Dinitrotoluene, when heated with bromine in sealed tubes at 150°, forms 2 : 6-dinitrobenzyl bromide; this is condensed with aniline to 2 : 6-dinitrobenzylaniline, and the product oxidised with permanganate to 2 : 6-dinitrobenzylideneaniline, which on warming with dilute acids is hydrolysed to 2 : 6-dinitrobenzaldehyde and aniline.

Steric hindrance was not observed with 2 : 6-dinitrobenzaldehyde, which condenses with phenylhydrazine, hydroxylamine, and aniline or with acetic acid to 2 : 6-dinitrocinnamic acid. The 2 : 6-dinitrobenzonitrile could not be hydrolysed by boiling with concentrated hydrochloric acid. 2 : 6-Dinitrocinnamic acid does not form an additive product with bromine.

2 : 6-*Dinitrobenzyl bromide* separates in somewhat brown, well-formed crystals, m. p. 81°. 2 : 6-*Dinitrobenzylaniline* forms yellowish-red needles, m. p. 108°; it is decomposed by sunlight, rapidly becoming dark red. The *platinichloride* crystallises in yellow needles.

Dinitrobenzyl bromide also condenses with *p*-anisidine, *α*-naphthylamine, and anthranilic acid, forming respectively the compounds: $C_6H_3(NO_2)_2 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot OMe$, bright red, slender needles grouped in bunches, m. p. 119°; $C_6H_3(NO_2)_2 \cdot CH_2 \cdot NH \cdot C_{10}H_7$, red needles, m. p. 154°; and $C_6H_3(NO_2)_2 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot CO_2H$, yellow needles, m. p. 199°.

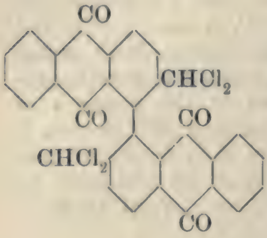
2 : 6-*Dinitrobenzylideneaniline* crystallises in very slender, pale yellow needles, m. p. 131°.

2 : 6-*Dinitrobenzaldehyde* crystallises in slender, colourless platelets, m. p. 123°. The *phenylhydrazone* crystallises in dark red needles, m. p. 159°; the *oxime* separates in colourless needles, m. p. 115°. 2 : 6-*Dinitrobenzonitrile* forms faint brown-coloured needles, m. p. 145°.

2 : 6-*Dinitrocinnamic acid* crystallises in colourless needles, m. p. 181°; the *ethyl* ester separates in slender needles, m. p. 82°. E. F. A.

Preparation of Aldehydes in the Anthraquinone Series. Badische Anilin- & Soda-Fabrik (D.R.-P. 240834. Compare Abstr., 1907, i, 327, 539, 942).—When the halogenated dimethyldianthra-

quinonyl (annexed formula) or its derivatives are heated with concentrated sulphuric acid either with or without the addition of sulphur trioxide or boric acid, they yield the corresponding dianthraquinonyldialdehydes.



The following compounds have been prepared: 4 : 4′-*Dichloro*-1 : 1′-*dianthraquinonyl*-2 : 2′-*dialdehyde*, golden-yellow leaflets from ωωωω-4 : 4′-*hexachloro*-2 : 2′-*dimethyl*-1 : 1′-*dianthraquinonyl*, m. p. above 320°, which was obtained by chlorinating 4 : 4′-dichloro-2 : 2′-dimethyl-1 : 1′-dianthraquinonyl in the side-chain.

ωωωω-6 : 6′-*Hexachloro*-2 : 2′-*dimethyl*-1 : 1′-*dianthraquinonyl*, m. p. 188—191°.

ω-*Tetrabromo*-2 : 2′-*dimethyl*-1 : 1′-*dianthraquinonyl*, decomp. 330° (about).

ω-*Tetrachloro*-2 : 2′-*dimethyl*-1 : 1′-*dianthraquinonyl*, m. p. 302—305°.

The tinctorial properties of these substances are tabulated in the original. F. M. G. M.

Preparation of Condensation Products in the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 241472. Compare preceding abstract).—When 1-chloroanthraquinonyl-2-aldehyde (or its substituted derivatives) is heated with halogen eliminating agents (such as copper) in nitrobenzene or naphthalene solution, condensation occurs, yielding 1 : 1′-*dianthraquinonyl*-2 : 2′-*dialdehyde* (formula I), which can be crystallised from *o*-dichlorobenzene.

The preparation of 6 : 6′-*dichloro*-1 : 1′-*dianthraquinonyl*-2 : 2′-*di*-

(I.)

(II.)

aldehyde (formula II) and other analogous compounds is described in the original. F. M. G. M.

Reversible Transformation of Many Carboxylic Acids into Keten-Hydrates. ERNST MOHR (*J. pr. Chem.*, 1912, [ii], 85, 334—336).—The author refers to the researches of Fischer and Dilthey (Abstr., 1902, i, 269) on the formation of amides from esters of alkylmalonic acids, and to the investigations of Kelber (Abstr., 1910, i, 390) on phenyl ββ-dithiolvinyl ketone in support of the view recently developed by Aschan (this vol., i, 198) that in

certain circumstances carboxylic acids may undergo a reversible transformation into keten-hydrates, $>CH\cdot CO_2H \rightleftarrows >C\!:\!C(OH)_2$, and gives an explanation of the interconversion of the stereoisomeric β-nitro-α-methoxy-$\alpha\beta$-diphenylethanes (Heim, Abstr., 1911, i, 717) similar to that adopted by Aschan to account for the transformation of geometric isomerides. F. B.

Zinc Chloride as Condensing Agent. GUSTAV REDDELIEN (*Annalen*, 1912, **388**, 165—199).—Benzophenone, fluorenone, benzoin, or benzil does not react with aniline at 160°. After the addition of a little zinc chloride (1/40 mol.), however, a violent evolution of steam is observed, and a good yield of the anil is obtained, the zinc chloride being recovered in the form of the double compound,

$$2NH_2Ph,ZnCl_2.$$

Similar phenomena are observed with the toluidines, xylidines, phenylenediamines, anisidine, and phenetidine, all of which form double compounds, $2NH_2Ar,ZnCl_2$, but not with the nitroanilines, aminophenols, or benzidine, which do not form double compounds with zinc chloride. It is clear, therefore, that the condensation is due to the catalytic influence of the double compound. It is unlikely that the double compound is the direct cause of the elimination of water, because these compounds are stable and are not hygroscopic. Now Dimroth and Zoeppritz have shown that the formation of benzophenoneanil occurs in two stages, the intermediate product,

$$OH\cdot CPh_2\cdot NHPh$$

(which can be isolated in the form of the hydrochloride), being very unstable and easily losing water. At 160°, this decomposition will proceed extremely rapidly. The increased rate of formation of the anil in the presence of zinc chloride, therefore, must be due to an acceleration of the first stage of the reaction: $COPh_2 + NH_2Ph = OH\cdot CPh_2\cdot NHPh$. It can be shown experimentally that the double compound, $2NH_2Ar,ZnCl_2$, loses a portion of its amine at 160°, even in the presence of an excess of the amine. Moreover, zinc chloride can combine, not only with amines, but also with ketones, to form well-characterised additive compounds. These additive compounds react with aniline at 160° to form the anil and steam. Equivalent quantities of the free ketone and the zinc chloride-aniline compound do not yield the anil at 160°; the presence of an excess of aniline is necessary. This excess is required for the formation of the compound $\begin{matrix}Ph_2CO\\(PhNH_2)_2\end{matrix}\!\!>ZnCl_2$. Consequently the formation of the anil is the result of four successive reactions:

(1) $ZnCl_2 + 2NH_2Ph = 2NH_2Ph,ZnCl_2$.

(2) $COPh_2 + 2NH_2Ph,ZnCl_2 = \begin{matrix}COPh_2\\(NH_2Ph)_2\end{matrix}\!\!>ZnCl_2$.

(3) $\begin{matrix}COPh_2\\(NH_2Ph)_2\end{matrix}\!\!>ZnCl_2 + NH_2Ph = OH\cdot CPh_2\cdot NHPh + 2NH_2Ph,ZnCl_2$.

(4) $OH\cdot CPh_2\cdot NHPh = CPh_2\!:\!NPh + H_2O$.

Reactions (1) and (4) occur instantly, (2) and (3) require several minutes.

The formation of the anil is never complete, even after heating

benzophenone, aniline, and zinc chloride at 160° for one hour, some unchanged ketone and amine are recovered. Probably the system $COPh_2 + NH_2Ph \rightleftarrows CPh_2{:}NPh + H_2O$ attains a state of equilibrium. Since the zinc chloride (or zinc chloride-aniline) accelerates the formation of the anil, it must also accelerate its decomposition. This is found to be the case. Benzophenoneanil is decomposed very slowly by water at 180—200°, but at about 165° in the presence of a little zinc chloride-aniline the hydrolysis is complete in thirty minutes.

Acetophenone and aniline do not yield acetophenoneanil even in the presence of the usual condensing agents. With zinc chloride, the ketone condenses with itself, and yields dypnone and *s*-triphenylbenzene. An explanation of this is found in the facts that acetophenone and aniline at 160° yield acetophenoneanil in thirty minutes in the presence of zinc chloride-aniline, but give 60% of *s*-triphenylbenzene in three to four minutes in the presence of aniline hydrochloride (or hydrobromide, hydriodide, sulphate, nitrate, phosphate, or thiocyanate). When zinc chloride is employed as the condensing agent, therefore, a little hydrochloric acid, present in the zinc chloride or produced by a by-reaction, forms aniline hydrochloride, and this catalyst stimulates the second rapid condensation more than does the zinc chloride-aniline the first, slower reaction.

In the formation of the anil, acetophenone probably reacts in the keto-form, because benzophenone and fluorenone yield anils under the same conditions. In the formation of *s*-triphenylbenzene, acetophenone reacts apparently in the enolic form, $CH_2{:}CPh{\cdot}OH$, because, under similar conditions, only ketones which are capable of enolising react to form *s*-trisubstituted benzenes; benzophenone and aniline do not react at 160° in the presence of aniline hydrochloride. The following anils have been prepared by heating the ketone and the amine at 160—180° with a little zinc chloride-amine, $ZnCl_2,2NH_2Ar$: *acetophenone*-p-*tolil*, b. p. 181—183°/16 mm. (*s*-triphenylbenzene and *dypnone*-p-*tolil* (?), m. p. 110°, are obtained as by-products); *acetophenone*-m-*tolil*, b. p. 181—182°/13 mm.; *acetophenone*-p-*anisidil*, $CPhMe{:}N{\cdot}C_6H_4{\cdot}OMe$, m. p. 86°; *benzophenone*-p-*anisidil*, m. p. 70°. *Fluorenone zinc chloride*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>CO,ZnCl_2$, blackish-red needles, m. p. 333—334° (decomp), and *benzophenone zinc chloride*,

$$Ph_2CO,ZnCl_2,$$

yellowish-brown oil, are obtained by adding the ketone to a suspension of zinc chloride in benzene. Each is converted into aniline-zinc chloride by aniline at the ordinary temperature. At 163°, benzophenone-zinc chloride and aniline yield benzophenoneanil, whilst aniline-zinc chloride and benzophenone do not visibly react.

Zinc chloride and phenylhydrazine form an additive compound,

$$2NHPh{\cdot}NH_2,ZnCl_2,$$

which catalytically accelerates the reaction between ketones and phenylhydrazine; thus benzophenonephenylhydrazone is obtained from benzophenone and phenylhydrazine at 125° in 28% yield without, and in 73% yield with, the presence of a little of the additive compound. At 175° phenylhydrazine-zinc chloride is converted into

ammonia, aniline-zinc chloride, and benzene, produced by the oxidation of a portion of the phenylhydrazine. When a suitable substance is present, it can be oxidised in the course of the preceding decomposition; thus acetophenoneanil is converted smoothly into 2-phenylindole. In the light of these facts, an explanation is given of the course of Fischer's indole syntheses from hydrazones by means of zinc chloride at 180°.

The catalytic influence of metallic salts other than zinc chloride, on the condensation of benzophenone and aniline, has been studied. It is found that zinc chloride, bromide, and iodide are about equally effective, and cadmium iodide somewhat less so; that cadmium chloride, nickel chloride, and cupric chloride have very little influence; that zinc thiocyanate, cadmium bromide, manganese chloride, and cobalt chloride exert an influence intermediate between that of the two preceding classes; and that mercury chloride, calcium chloride, magnesium chloride, and aluminium chloride have no catalytic influence at all. C. S.

Propiophenone Derivatives. F. W. Calliess (*Arch. Pharm.*, 1912, **250**, 141—154).—These products were obtained in the course of attempts to synthesise substances having the formula ascribed by Schmidt and Bümming to ephedrine and ψ-ephedrine (Abstr., 1909, i, 322). Comparison of the α-aminopropiophenones prepared by Schmidt's method (Abstr., 1890, 372) and by that of Behr-Bregowski (Abstr., 1897, i, 458) shows that the two are identical.

The following derivatives of α-aminopropiophenone were prepared: hydrochloride, slender needles, m. p. 179°; nitrate, columnar crystals, m. p. 139—140°; *aurichloride*, yellow needles, m. p. 151°; *mercurichlorides*, $B,HCl,2HgCl_2,H_2O$, slender, colourless needles, m. p. 126°, and $B,HCl,HgCl_2$, colourless, dull needles, m. p. 165°; *stannichloride*, $B_2H_2SnCl_6$, m. p. 219—220°. On reduction with sodium amalgam in acid solution the amino-ketone yields *phenylaminoethylcarbinol*, $OH\cdot CHPh\cdot CHMe\cdot NH_2$, m. p. 101°, which separates from ether in yellow crystals, and gives a *hydrochloride*, m. p. 191°, colourless needles, a *platinichloride*, $B_2,H_2PtCl_6,2H_2O$, m. p. 187—188°, yellowish-red needles, and an *aurichloride*, $B,HAuCl_4$, m. p. 130°, silky, yellow needles. On methylation the amino-alcohol gives a mixture of methylated products, from which the quaternary base,

$$OH\cdot CHPh\cdot C_2H_4\cdot NMe_3,$$

was isolated in the form of its aurichloride, $BCl,AuCl_3$, m. p. 171—172°, yellow leaflets, and of its platinichloride, m. p. 245—247° (decomp.), slender needles, the latter being probably identical with the salts prepared in another manner by Göhring (Abstr., 1909, i, 322).

α-Aminopropiophenone on methylation yields a mixture of tertiary and quaternary bases. The former yields an *aurichloride*,

$$C_6H_5\cdot CO\cdot C_2H_4NMe_2,HAuCl_4,$$

m. p. 152°, small leaflets. The quaternary base has been prepared already by Göhring (*loc. cit.*). T. A. H.

4'-Nitro-2:5-dimethoxybenzophenone. Hugo Kauffmann and Albrecht de Pay (*Ber.*, 1912, **45**, 776—780).—*4'-Nitro-2:5-dimethoxybenzophenone*, m. p. 126°, obtained from *p*-nitrobenzoyl chloride,

quinol dimethyl ether, and aluminium chloride in carbon disulphide, forms yellow crystals, and is therefore an example of a constitutively unchangeable nitro-compound which exhibits colour. By oximation in alcoholic solution in the presence of sodium acetate, it yields two *oximes*; the more soluble one has m. p. 145°, forms a *benzoate*, m. p. 158°, white leaflets, and is also produced by prolonged heating in toluene of the less soluble *oxime*, m. p. 195° (*benzoate*, m. p. 150°, yellow crystals). 4'-*Nitro*-2 : 5-*dimethoxybenzophenonephenylhydrazone* exists in three modifications, having m. p. 165°, 145°, and 81° respectively. The first two are obtained from the ketone and phenylhydrazine in glacial acetic acid, and are converted at their m. p.'s into the third modification. This modification changes into the first by prolonged heating on the water-bath, and into the second by crystallisation from alcohol. It is probable that two of these modifications are stereoisomerides, the remaining one being a polymorphous form of one of the others; which is which, it is impossible to say. C. S.

Dissociation of Quinhydrone in Aqueous Solution. ROBERT LUTHER and A. LEUBNER (*J. pr. Chem.*, 1912, [ii], **85**, 314—321).—The dissociation of quinhydrone has been studied by determining its solubility in water, and also in aqueous solutions of quinone and quinol. At 25° in a saturated solution, quinhydrone is dissociated to the extent of 93%; the solubility of the undissociated quinhydrone is $1{\cdot}3 \times 10^{-3}$ gram-mol. per litre.

The dissociation constant, K = quinhydrone × quinol/quinhydrone at 25° = 0·23. F. B.

Action of Copper on Chloroanthraquinones. FRITZ ULLMANN and WASSILY MINAJEFF (*Ber.*, 1912, **45**, 687—690).—Some chlorinated anthraquinones lose their halogen, and are converted into anthraquinones by treatment with copper powder and potassium acetate; thus 1-chloro-4-methylanthraquinone, potassium acetate, and a little copper powder react in boiling nitrobenzene to form 1-methylanthraquinone and a very little 4 : 4'-*dimethyl*-1 : 1'-*dianthraquinonyl*, $C_6H_4{<}{}^{CO}_{CO}{>}C_6H_2Me{\cdot}C_6H_2Me{<}{}^{CO}_{CO}{>}C_6H_4$, m. p. 385—386°, yellow plates. The latter becomes the chief product when 1-chloro-4-methylanthraquinone is heated in nitrobenzene with copper powder (1 atom) alone. Scholl and Mansfeld's 1 : 1'-dianthraquinonyl is obtained in 75% yield by heating 1-chloroanthraquinone with copper powder in nitrobenzene; a 77% yield can be obtained by heating the two substances at 290—300° without nitrobenzene.

Chloroanthraquinones, which contain the halogen in position 2, are unattacked by copper powder. C. S.

Constituents of Essential Oils. A New Primary Alcohol of the Sesquiterpene Series, Cedrenol, $C_{15}H_{24}O$. FRIEDRICH W. SEMMLER and ERWIN W. MAYER (*Ber.*, 1912, **45**, 786—791).—Cedar wood oil contains in addition to solid cedrol, $C_{15}H_{26}O$, m. p. 85°, a primary alcohol, cedrenol, $C_{15}H_{24}O$, which is tricyclic and contains one unsaturated linking. *Cedrenol* constitutes about 3% of the oil; it

has b. p. 161—167°/10 mm., D^{20} 1·0098, $[\alpha]_D^{20} + 1°$, n_D^{20} 1·523. The *acetate* is a colourless, odourless liquid, b. p. 165—169°/9 mm., D^{20} 1·0168, n_D^{20} 1·5021, $[\alpha]_D^{20} - 2°$; the pure cedrenol obtained from it on hydrolysis is optically inactive.

Cedrenyl chloride, $C_{15}H_{23}Cl$, is a colourless liquid, b. p. 150—165°/10 mm., D^{20} 1·001.

Cedrene, $C_{13}H_{20}{<}\genfrac{}{}{0pt}{}{CMe}{\overset{||}{CH}}$, the corresponding hydrocarbon, obtained by reduction of the chloride with sodium and alcohol, has b. p. 117—130°/7 mm., D^{20} 0·931, n_D 1·5080, $[\alpha]_D^{20} - 3°$ to $+13°$, according to the method of preparation. On decomposition of cedrene ozonide, cedrene ketonic acid was obtained, identical with that described by Semmler and Risse (this vol., i, 201), and this, on further oxidation, yielded cedrenedicarboxylic acid (Semmler and Risse, *loc. cit.*).

Cedrenol contains a $CH_2 \cdot OH$ group in the same position as the CH_3 group is situated in cedrene and cedrol. E. F. A.

Production of Formic and Acetic Acid by the Atmospheric Oxidation of Turpentine. CHARLES T. KINGZETT and REGINALD C. WOODCOCK (*J. Soc. Chem. Ind.*, 1912, **31**, 265—267).—It is shown that turpentine, pinene, and sylvestrene yield formic and acetic acids and hydrogen peroxide when submitted to atmospheric oxidation. It has not yet been ascertained definitely whether the hydrogen peroxide, the acetic acid, and the formic acid severally depend for their production on the interaction of water on one organic peroxide only, or more than one, but the authors favour the view that one organic peroxide alone is formed, and at the same time formaldehyde and acetaldehyde, the two latter substances being converted into their corresponding acids when the organic peroxide yields hydrogen peroxide on being placed in contact with water. W. P. S.

The Oxidation of Camphene. OSSIAN ASCHAN (*Chem. Zentr.*, 1912, i, 415—416; from *Öfver. Finska Vet. Soc. Förhandl.*, 1911, **53**, Afd. A, 1—18).—When terecamphene vapour mixed with air is passed over heated spongy platinum, an oily liquid is obtained, in which the presence of benzene and *m*-xylene can be established. The gaseous products contain much carbon dioxide.

By oxidation of terecamphene dissolved in glacial acetic acid by means of solid potassium permanganate, a mixture of neutral and acid compounds is obtained. Among the former are *camphenilone*, b. p. 80—84°/14 mm. (which yields a *semicarbazone*, m. p. 222—223°), a small quantity of a *substance*, $C_9H_{14}O$, b. p. 87—90°/14 mm., which gives the aldehyde reaction with ammoniacal silver nitrate, does not yield a semicarbazone, does not solidify at $-15°$, and when exposed to air in the presence of water forms a monobasic *acid*, $C_9H_{14}O_3$, m. p. 136—137°, and finally a *substance*, b. p. 143—150°/14 mm., which when freshly distilled has no acid reaction, but when preserved during several days deposits needles or leaflets of an unsaturated monobasic *acid*, $C_7H_{11} \cdot CO_2H$, m. p. 141°.

From the acidic products, an oil, b. p. 148—150°/10 mm., 153°/14 mm., was isolated, which gradually partly solidified. After removal

of unsaturated substance by oxidation with potassium permanganate in alkaline solution, two isomeric acids, $C_{10}H_{16}O_2$, were obtained. The first, *camphenanic acid*, m. p. 87—91°, is monobasic, and forms a *calcium* salt, $(C_{10}H_{15}O_2)_2Ca,5H_2O$. The second, iso*camphenanic acid*, has m. p. 75—76°. Neither acid appears to be identical with Bredt's camphenilanic acids, nor to be the racemic form of these acids.

H. W.

Sesquiterpenes. V. ERNST DEUSSEN (*Annalen*, 1912, **388**, 136—165. Compare Abstr., 1910, i, 575).—[With BENNO EGER.]—By passing nitrous fumes into an ethereal solution of caryophyllene, a voluminous precipitate is obtained of a substance, $C_{12}H_{19}O_6N_3$, m. p. 159·5°, $[\alpha]_D$ − 133°50′, which is identical with one of the two substances obtained by the decomposition of β-caryophyllene nitrosite by heat (Abstr., 1907, i, 945). So voluminous is the precipitate and so slight its solubility in most solvents, that the reaction furnishes an excellent method for the detection of β-caryophyllene. Two fractions, b. p. 127—128·5°/14 mm. and 118·5—122°/11·5 mm. respectively, of caryophyllene from oil of cloves were found to contain 25—27% of β-caryophyllene by this method. Oils of Para- and of Maracaibo-copaiva balsams contain 5·15 and 2·0% respectively of β-caryophyllene. The sesquiterpenes obtained by the distillation with steam of oil of African copaiva balsam can be separated into two fractions, one, b. p. 145·5—148°/19·5 mm., consists largely of *d*-cadinene, and the other, b. p. 128—129·5°/15 mm., contains 13·2% of β-caryophyllene. Oil of West Indian sandal-wood contains 30—40% of sesquiterpenes, in which *d*-cadinene and β-caryophyllene have been detected.

[With MAX ZIEM.]—According to Chapman (Trans., 1895, **67**, 61, 780; 1903, **83**, 505), oil of hop blossoms contains a terpene (subsequently identified as myrcene) and a sesquiterpene called humulene. The latter consists essentially of *i*-α-caryophyllene, but is shown to contain about 4% of β-caryophyllene by the nitrous fumes method.

[With KURT MEYER.]—The sesquiterpene regenerated from β-caryophyllene dihydrochloride by means of methyl-alcoholic potassium hydroxide is not *iso*caryophyllene, but is probably a mixture, because it gives only a 25% yield of β-caryophyllene dihydrochloride and forms an amorphous nitrosochloride, from which a *nitrolbenzylamine*, m. p. 162°, not identical with β-caryophyllenenitrolbenzylamine, m. p. 166—167°, is obtained. *iso*Caryophyllene, obtained by boiling an alcoholic solution of β-caryophyllene nitrosite, gives a 100% yield of α- and β-nitrosochlorides, and a 73% yield of β-caryophyllene dihydrochloride. It is probable that the constitutions of β-caryophyllene and of *iso*caryophyllene differ only in that the former contains the group $>C\colon CMe_2$, whereas the latter contains the group

$$>CH\cdot CMe\colon CH_2.$$

[With C. VIELITZ.]—The following experiments were undertaken to show the presence of two double linkings in α- and β-caryophyllenes. A purified sample, b. p. 130—131°/16·5 mm., α − 7°40′ (consisting chiefly of β-caryophyllene, together with a little α-caryophyllene), diluted with 2 vols. of methyl alcohol, is treated with colloidal palladium and saturated with hydrogen. The product is a *dihydro-*

caryophyllene, $C_{15}H_{26}$, b. p. 129—130°/14 mm., $\alpha - 25°$, D^{19} 0·8898, n_D^{20} 1·49032. Since the following experiments prove that two double linkings are present in caryophyllene, it follows that they are functionally different, only one of them being saturated by hydrogen. A solution of α-caryophyllene nitrosochloride in cold chloroform absorbs 2 atoms of bromine, yielding probably an unstable dibromide, which changes to a *hydrobromocaryophyllene nitrosochloride*,

$C_{15}H_{25}Br,NOCl$,

m. p. 144—145° (decomp.), colourless needles. A suspension of β-caryophyllene nitrosite in methyl alcohol is treated with colloidal palladium and saturated with hydrogen in darkness, whereby a *substance*, $C_{15}H_{26}O_3N_2$ or $C_{15}H_{28}O_3N_2$, m. p. 99—100°, is obtained, which readily decolorises bromine; consequently the addition of the hydrogen has occurred at the NO or the O·NO group. By saturating an ethereal solution of β-caryophyllene nitrosite with hydrogen chloride at $-20°$ to $-15°$, *β-hydrochlorocaryophyllene nitrosite*,

$C_{15}H_{25}O_3N_2Cl$,

m. p. 137° (decomp.), $[\alpha]_D$ $+930·4°$ in benzene, is obtained in dark blue needles. The formation of this compound, not only proves the presence of the two double linkings in β-caryophyllene, but is also a strong support of Baeyer's theory that the blue colour of nitrosochlorides, nitrosites, and nitrosates is due to the union of the NO group with a tertiary carbon atom.

By treating β-caryophyllene nitrosite, β-caryophyllene nitrosochloride, or *iso*caryophyllene nitrosochloride with alcoholic potassium hydroxide, a dextrorotatory, crystalline *substance*, $C_{17}H_{29}O_2N$, m. p. 163°, containing an ethoxy-group is obtained. C. S.

Essential Oils. SCHIMMEL & Co. (*Bericht*, April 1912, pp. 22—133).—*Acronychia laurifolia* leaves furnish an oil having the following constants: D^{26} 0·915, $[\alpha]_D$ $+1°52'$, saponification number 11, acetyl ester number 50·9, and free from aldehydes.

Inula helenium roots yield a semi-solid oil, D^{30} 1·0374, $[\alpha]_D$ $+123°45'$, n_D^{20} 1·52208, acid number 6·4, ester number 180, and after acetylation 199, consisting of colourless needles in a brown, viscous liquid, and having an odour recalling that of ladanum.

Artemisia frigida herb grown in South Dakota yields, according to Rabak, 0·26% of oil, D^{24} 0·940, $[\alpha]_D$ $-24·2°$, n_D^{24} 1·4716, acid number 2·5, ester number 25, after acetylation 139, containing *l*-borneol, cineole, *l*-fenchone, probably heptoic and octoic acids, valeric acid, and traces of formic and undecoic acids. The total borneol amounts to 43%, of which 35·6% is in the free state.

Camphor leaves, distilled in Jamaica, yielded 2·35% of crude camphor, consisting of camphor 1·32%, camphor oil 0·54%, and moisture 0·49%. Camphor twigs gave 0·58% of camphor and 0·26% of camphor oil, whilst the wood yielded 0·61% of camphor. The oil contained, in addition to camphor, cineole, safrole, pinene, phellandrene, and dipentene.

"Cape" leaves from the Ivory Coast, according to Roure-Bertrand Fils, furnish 0·28% of a greenish-yellow oil, D^{15} 0·977, $[\alpha]_D$ $+39°$ 38′,

acid number 0·7, saponification number 109·2, soluble in its own volume of 80% alcohol, and having a patchouli odour.

Cedrela odorata wood, according to Rabak, gives 0·3% of a golden-yellow oil, D^{25} 0·947, n_D^{25} 1·5038, acid number 3·9, ester number 41·5, after acetylation 51, which is soluble in six volumes of 80% alcohol.

Ceylon citronella oil has been shown previously to contain citronellal, camphene, dipentene, methylheptenone, borneol, geraniol, methyleugenol, *l*-limonene, together with acetic and valeric acids as esters. A dextrorotatory sesquiterpene and possibly linalool have also been found. It is now shown that the following constituents are also present: *d*-citronellol in the form of its acetic and *n*-butyric esters, geranyl acetate, thujyl alcohol, nerol, an *alcohol* closely related to linalool, a *hydrocarbon*, $C_{10}H_{16}$, D^{15} 0·8323 to 0·8360, $[\alpha]_D - 23°24'$ to $-32°41'$, n_D^{20} 1·48044, b. p. 40—41°/4 mm., having a tarragon-like odour, and a lævorotatory sesquiterpene. Linalool and valeric acid could not be found.

Cymbopogon intermedius, distilled in Buitenzorg, gave 0·03% of oil, D^{26} 0·919, $[\alpha]_D$ $-15°30'$, and *C. odoratus* from the same source furnished 0·35% of oil, D^{26} 0·914, $[\alpha]_D - 31°10'$.

American spearmint, grown in Michigan, according to Nelson, gave an oil, D_{25}^{25} 0·9290, $[\alpha]_D^{25}$ $-52°16'$, n_D^{25} 1·4866, ester number 12·4, which contained 66% of carvone, together with phellandrene, *l*-limonene, and the acetic ester of dihydrocarveol. The oil also contains hexoic or octoic acid, butyric acid (?), with 0·1% of a solid acid, m. p. 182—184° (compare Elze, Abstr., 1910, i, 865).

Linaloe wood from Cayenne furnished, in addition to the oil, distillation water containing furfuraldehyde, *iso*valeraldehyde (?), linalool, methylheptenol, cineole, dipentene, and an aliphatic terpene, myrcene (?), which on hydration with acetic and sulphuric acids gave an ester, that on hydrolysis yielded an alcohol having an odour of linalool and terpineol.

Magnolia glauca leaves, according to Rabak, yield 0·05% of a yellow oil, D^{25} 0·9240, $[\alpha]_D$ $+3·96°$, n_D^{25} 1·4992, acid number 1·8, ester number 13, and after acetylation 28, which is insoluble in 80% alcohol.

Melaleuca trichostachya leaves furnish 1·25 to 2·58% of oil, D^{15} 0·9144 to 0·9153, $[\alpha]_D$ + 2·3° to 3·1, n_D^{20} 1·4636 to 1·4655, saponification number 2·1 to 2·8, acetyl ester number 13·9, soluble in 1·3 volumes of 70% alcohol, and containing cineole 80%, terpineol, terpinyl acetate, pinene (?), sesquiterpene (?), with traces of phenols and a low-boiling aldehyde. *M. bracteata* leaves and twigs gave 0·643 to 0·964% of an oil, D^{18} 1·032 to D^{19} 1·0358, $[\alpha]_D - 1·4°$ to 3·1°, n_D^{20} 1·5325 to 1·535, acid number 0·7 to 1·26, saponification number 5·3 to 20·8, soluble in 0·7 to 0·8 volumes of 70% alcohol, and containing eugenol, free and combined cinnamic acid, cinnamaldehyde, methyleugenol, 70%, cinnamyl cinnamate (?), and *l*-phellandrene (Baker and Smith, *J. Roy. Soc. New South Wales*, 1911, **44**, 592).

Micromeria japonica herb, according to Muragama, yields 0·7% of a yellow, peppermint-like oil containing *l*-menthone and menthol (?).

Nepeta nepetella herb furnishes 0·059% of a viscid, yellow oil, D^{20} 1·03984, $[\alpha]_D$ $+15°12'$, acid number 45·5, ester number 245·7, after

acetylation 314·5, soluble in two volumes of 70% alcohol, which deposits a solid substance with an odour of menthol, and on hydrolysis furnishes octoic and valeric acids.

Persea pubescens leaves, according to Rabak, yield 0·2% of oil, D^{25} 0·9272, $[\alpha]_D$ +22·4°, n_D^{25} 1·4695, acid number 2·8, ester number 14·5, after acetylation 64, soluble in 0·3 volume of 80% alcohol, containing free butyric acid with butyric, valeric, and heptoic acids as esters, together with *d*-camphor, cineole, and small quantities of borneol and formaldehyde.

Japanese peppermint oil yielded a fraction, b. p. 175—181°, containing *d*-ethyl-*n*-amylcarbinol, $C_5H_{11}\cdot CHEt\cdot OH$.

Pluchea foetida herb, according to Rabak, yields 0·025% of a golden-yellow oil, D 0·9329, $[\alpha]_D$ −5·4° (50 mm. tube), n_D^{23} 1·4845, acid number 4·1, ester number 44, after acetylation 104, soluble in one volume of 80% alcohol and containing cineole.

Ramona stachyoides herb yields, according to Rabak, 0·75% of a colourless oil, D^{24} 0·9144, $[\alpha]_D$ +30·2°, n_D^{24} 1·4682, acid number 2, ester number 2·5, after acetylation 27·1, soluble in 1·5 volumes of 70% alcohol, which deposits *d*-camphor when kept at −15°, and contains cineole, and probably borneol, tanacetone, and pinene with acetic acid and traces of formic acid.

Satureja montana oil, distilled in Southern France, had D^{15} 0·908 to 0·9194, $[\alpha]_D$ −1°42′ to 4°48′, and contained 27 to 32% of carvacrol (compare Pickles, Proc., 1911, 27, 285).

Aframonum angustifolium seeds from German East Africa gave 4·5% of a colourless oil, D^{15} 0·9017, $[\alpha]_D$ −16°50′, n_D^{20} 1·46911, acid number 0·4, ester number 4·2, soluble in 6 or more volumes of 80% alcohol and containing much cineole. T. A. H.

The Essential Oil from Rhizoma Imperatoriæ. FRITZ LANGE (*Chem. Zentr.*, 1912, i, 654; from *Arb. Pharm. Inst. Univ. Berlin*, 1911, 8, 98—120).—The oil obtained by distillation with steam is a greenish-yellow liquid, D^{15} 0·8659, $[\alpha]_D^{14}$ +69·75°, acid number 0·8, saponification number 17·9, ester number after acetylation 28·34. It consists of a mixture of free acids, alcohols, esters, terpenes, and sesquiterpene, terpenes constituting about 95% of the oil. Palmitic acid is contained among the free acids; acetic, formic, *iso*butyric, *iso*valeric, and ββ-dimethylacrylic acids are present in the form of esters. The terpenes present include pinene, dipentene, *d*-limonene, *d*-phellandrene, chiefly the latter. The sesquiterpene yields a crystalline *dihydrochloride*, m. p. 157—157·5°. The oil also contains an *alcohol*, the formula of which is probably $C_{10}H_{19}\cdot OH$, which yields a *phenylurethane*, m. p. 145—146°. H. W.

The Essential Oil of the Catkins of Wild Myrtle (Myrica Gale). C. J. ENKLAAR (*Chem. Weekblad*, 1912, 9, 219—222. Compare Pickles, Trans., 1911, 99, 1764).—The oil obtained from the catkins of wild myrtle is a viscid, yellow liquid, and with a characteristic odour. It has D^{15} 0·899, and $[\alpha]_D$ −5°36′. About 80% of it consists of terpenes, of which a pinene and a sesquiterpene, $C_{15}H_{24}$, constitute about 40%. It also contains cineole, phellandrene, and a small proportion of a *substance* not identified, which crystallises in long needles

and has a myrtle-like odour. The sesquiterpene probably contains caryophyllene. It has b. p. 150—152°/17 mm. or 263—265°/760 mm., and $[\alpha]_D$ +4°30′. A. J. W

Minjak Lagam. LEOPOLD VAN ITALLIE and MAX KERBOSCH (*Pharm. Weekblad*, 1912, **49**, 274—279).—The volatile oil obtained from the liquid variety of Minjak lagam is caryophyllene. The semi-solid form yields the same substance. A. J. W.

Oleo-resin of Abies cephalonica. EMMANUEL J. EMMANUEL (*Arch. Pharm.*, 1912, **250**, 104—110).—The crude oleo-resin had acid number, direct 113·54, indirect 128·31; saponification number 137·06 (cold), 157·54 (hot), and was soluble in alcohol, ether, or chloroform.

From the ether solution 1% ammonium carbonate solution extracted *elatic acid*, $C_8H_{12}O_2$, m. p. 124—126°, and then 3% sodium carbonate solution removed a mixture of two acids, *elatinic acid*, $C_{12}H_{18}O_2$, m. p. 78—80°, which gives a lead salt insoluble in alcohol, and *elatolic acid*, $C_9H_{16}O_2$, m. p. 118—120°, the lead salt of which is soluble in alcohol. These products are amorphous, and the two latter together form 70% of the oleo-resin.

The residue, after the removal of the ether, was steam distilled, and yielded 17·4% of essential oil, D^{15} 0·9279, α_D −68° in 200 mm. tube, $n_D^{13\cdot5}$ 1·4745, which was colourless and on distillation yielded three fractions, b. p. 89—150°, 150—155°, 155—175°, of which the first two had a terpene-like odour.

The residual matter in the flask was amorphous *resen*, m. p. 92—96°, with water containing a bitter substance. The acids and the resen gave phytosterol reactions. T. A. H.

Cretan Ladanum. EMMANUEL J. EMMANUEL (*Arch. Pharm.*, 1912, **250**, 111—117).—Ladanum is a resinous exudation of Cistus, spp., that examined being from *Cistus creticus*. It was dark brown in colour, softened readily when worked in the fingers, and had a peculiar, pleasant odour with a balsamic, bitter pungent taste. It dissolved to the following amounts in the solvents named: ether 61%, chloroform 69%, alcohol 57%, and was practically insoluble in water or light petroleum. It contained 12·0% of ash.

The portion soluble in ether on extraction with sodium carbonate solution yielded a viscid, brown resin acid. The portion insoluble in ether, but soluble in alcohol, was a viscid, bright brown resin. An essential oil, D 0·928, b. p. 225°, $n_D^{13\cdot5}$ 1·5118, was obtained by steam distilling the residue of the ethereal extract after treatment with sodium carbonate solution. After the removal of the essential oil, a solid, crystalline substance, *ladaniol*, $C_{17}H_{30}O$, m. p. 89°, colourless prisms, began to distil over. This resembled champacol and guaiol (Wallach and Tuttle, Abstr., 1894, i, 538). The portion of ladanum insoluble in ether and alcohol contained (1) a bassorin-like gum, which gave mucic acid on oxidation with nitric acid; (2) a greyish-white, pulverulent resen, and (3) a bitter substance. T. A. H.

The Cerebrosides of the Brain. II. HERMANN LOENING and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1912, **77**, 202—217. Compare Abstr., 1911, i, 898).—The author's method of separating

cerebrosides from "protagon" depends on their resistance to barium hydroxide, and their solubility in hot acetone. After boiling cerebrone with baryta water for an hour, 90·4% was subsequently recovered in crystalline form; the loss may be due to the destruction of the cerebrone, or to its decomposition by alkali. In the present research, "protagon" was employed, and some evidence that barium compounds are formed is adduced; the loss on boiling with barium hydroxide is small, and was determined by estimating the yield of galactose after hydrolysis. Judged by this standard, from 93 to 97% of the cerebroside was recovered. A similar resistance to boiling with a 2·8% solution of potassium hydroxide containing methyl alcohol was also noted. The actual quantity of galactose obtained from the various preparations of protagon used varied from 6 to 13%. Thudichum's sphingosine was not obtained from cerebrone. The quantity of cerebroside obtained from protagon, taking into account the amount separated out from the acetone, as well as that which remained in solution, was about 39%. From dried brain powder, 2·13 grams of galactose were obtained; 73·2% of this passed into the alcoholic extract, and the remainder, which is an unexpectedly high amount, into the ethereal extract. W. D. H.

Cerebrone. V. OTTO RIESSER and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1912, **77**, 508—510).—On treatment of cerebrone with methyl alcoholic sulphuric acid, dimethylsphingosine, $C_{19}H_{39}O_2N$, was obtained (Kitagawa and Thierfelder, Abstr., 1907, i, 168). It is now shown that when ethyl alcohol is substituted, the corresponding *diethylsphingosine*, $C_{21}H_{43}O_2N$, is obtained. It forms a matted mass of lustrous platelets, m. p. 113—115°. The alkylsphingosines are accordingly not present in the cerebrone molecule, but are formed at the moment of hydrolysis; sphingosine, therefore, contains two hydroxyl groups. E. F. A.

Cerebrone. VI. KARL THOMAS and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1912, **77**, 511—515).—On acetylation of sphingosine either with acetyl chloride or acetic anhydride and sodium acetate, a *triacetate*, $C_{17}H_{32}O_2NAc_3$, is obtained; it crystallises in thin needles pointed at both ends, which soften at 98°, m. p. 99—100°. This characterises sphingosine as an unsaturated bivalent amino-alcohol.

The sparingly soluble sulphate of a base previously obtained (Kitagawa and Thierfelder, Abstr., 1907, i, 168) by the action of methyl-alcoholic sulphuric acid on cerebrone is now shown to be sphingosine contaminated with the dimethyl compound. E. F. A.

Glucosides of Digitalis purpurea Leaves. FRIEDRICH KRAFT (*Arch. Pharm.*, 1912, **250**, 118—141).—Schmiedeberg and, more recently, Kiliani in their investigation of digitalis constituents have used as a raw material "digitalinum germanicum," a mixture of substances prepared from digitalis seeds by extraction with alcohol and precipitation with tannin. From this material the following products have been obtained: Schmiedeberg's amorphous inactive digitonin, Kiliani's crystalline digitonin, Kiliani's digitalin, digitoxin, and

digitalein. As digitalis leaves are chiefly used in medicine, the author has examined them to ascertain whether they contain the constituents present in the seeds, and has obtained two new glucosides, gitalin and gitin, together with digitoxin. Schmiedeberg's amorphous digitonin is shown to be a mixture of saponins, which is also present in the leaves. In Keller's method for the valuation of digitalis leaves the product obtained is chiefly gitalin, with a little digitoxin (compare Burmann, this vol., ii, 379).

The leaves were extracted first with water and then with 50% alcohol, and the two extracts examined separately. The aqueous extract was defæcated in the usual way with lead acetate, followed by sodium phosphate, and the glucosides precipitated by tannin solution and recovered from the precipitate by mixing this with zinc oxide and extraction with methyl alcohol. The residue left on distilling off the solvent was dissolved in water and shaken repeatedly with chloroform, which extracted an active glucoside, gitalin, and left in solution a mixture of saponins. *Gitalin*, $C_{28}H_{48}O_{10}$, m. p. 150—155°, is a colourless, amorphous, neutral substance, soluble in most organic solvents, except light petroleum, and in 600 parts of water. When dissolved in 1·5 parts of alcohol to which 0·75 part of water is added, it separates as a crystalline *hydrate*, $C_{28}H_{48}O_{10},4H_2O$, m. p. 75°, soluble in 3000 parts of water, which is re-converted into the anhydrous form by drying over sulphuric acid. Solutions of gitalin are very unstable, and when kept deposit mixtures of gitalin with *anhydrogitalin*, $C_{28}H_{46}O_9$, m. p. 255°, which crystallises from diluted alcohol, is nearly insoluble in chloroform, and soluble in 800 parts of boiling alcohol. On hydrolysis by acids, all three substances yield (1) digitoxose, identical with the sugar obtained from digitoxin by Kiliani, and (2) *anhydrogitaligenin*, $C_{22}H_{34}O_5$, m. p. 216—219°, which crystallises from boiling alcohol in colourless plates.

The *digitosaponins*, obtained as described above, were freed from colouring matter by extraction with acetone, and then fractionated into α-, β-, and γ-saponins by extraction in turn with alcohol and methyl alcohol, γ-saponin being nearly insoluble in both these solvents. They are colourless, amorphous substances, which on hydrolysis by 5% sulphuric acid yield digitosapogenin and a pentose giving a phenylosazone, m. p. 156—158°. The most soluble α-saponin passes into the less soluble β- and γ-forms when boiled in alcohol. They appear to be identical with Schmiedeberg's digitonin.

The alcoholic extract, after treatment with lead acetate, was evaporated to a small bulk with calcium carbonate, cooled, filtered, and shaken out with ether, which removed lateolin. Digitoxin was then extracted with chloroform, and from the residue gitin was extracted by boiling alcohol. The digitoxin thus obtained contained gitalin, from which it was freed by repeated evaporation of an alcoholic solution, whereby the impurity was gradually converted into sparingly soluble anhydrogitalin. The purified digitoxin formed tabular crystals from boiling alcohol, melted sharply at 245°, and on hydrolysis yielded digitoxenin and digitoxose, but Kiliani's digitoxin hydrate could not be obtained by crystallisation from aqueous alcohol.

Gitin, m. p. 265° (decomp.), crystallises from alcohol in long, colour-

less needles, is soluble in 250 parts of boiling methyl alcohol or 120 parts of boiling alcohol, but is insoluble in water or chloroform. It is isomeric with Kiliani's digitonin, which it resembles in yielding digitogenin on hydrolysis, but differs from it in containing a galactose in place of a dextrose residue. It is physiologically inactive. Full experimental details are given in the original of the complicated processes used in isolating these substances, and their colour reactions with Keller's and Kiliani's reagents are recorded. T. A. H.

Constituents of Digitalis Leaves. RUDOLPH TAMBACH (*Pharm. Zentr.-h.*, 1912, **53**, 392—393).—From the precipitate obtained by the addition of tannin to a cold aqueous extract of digitalis leaves the author has isolated a substance called *digin*, m. p. 271—273°, colourless needles, which has little, if any, physiological activity, does not react with Kiliani's or Keller's reagent, and contains C 73·68% and H 10·33%. It presents points of similarity to Kraft's gitin (preceding abstract), but differs in its m. p., in its solubility in chloroform, and in its composition. The examination of the substance is being continued. C. S.

A Second Crystalline Compound of Phenolic Character from Fresh or Preserved Cola-nut. A. GORIS (*Chem. Zentr.*, 1912, i, 266; from *Bull. Sci. pharmacol*, **18**, 138—140. Compare Abstr., 1907, i, 631).—This compound, *collatein*, is insoluble in ether, chloroform, and light petroleum, but soluble in hot water, alcohol, and acetone. From water it separates with water of crystallisation in the form of needles, which effloresce over sulphuric acid; from anhydrous acetone and chloroform it separates in prisms, m. p. 257—258°. It is precipitated by lead acetate, gives a green coloration with ferric chloride, which turns blue on addition of ammonia, and does not set free carbon dioxide from carbonates. It has a bitter taste.

S. B. S.

"Peristaltin." ALEXANDER TSCHIRCH and L. MONIKOWSKI (*Arch. Pharm.*, 1912, **250**, 92—103).—"Peristaltin" is a patent preparation, used as a purgative, and obtained from the bark of *Rhamnus purshiana* (*Cascara sagrada*). It is a yellow, bulky powder, soluble in water or alcohol, partly in acetone, but insoluble in ether or light petroleum, and contains 4·2% water and 0·5% ash. It contains a reducing sugar, giving a phenylosazone, m. p. 208°. The substance appears to be a mixture of glucosides, and on hydrolysis by steam yields rhamnose, chrysophanic acid (chrysophanol), emodin methyl ether, and *cascarol*, together with a minute amount of a yellow colouring matter. When boiled with hydrochloric acid, peristaltin yields furfuraldehyde, and 2·06% of pentoses were found by Flint and Tollens' method. The product contains no nitrogenous substance.

Cascarol, $C_{15}H_{10}O_5$, m. p. 218°, forms yellow needles from pyridine or alcohol, is soluble in acetone or alcohol, insoluble in water, chloroform, ether, or cold sodium hydroxide solution, and yields a crystalline *acetyl* derivative, m. p. 204—205°.

The yellow colouring matter crystallises from hot water, melts at

203—204°, is soluble in alkalis, and gives a fluorescent solution in sulphuric acid. T. A. H.

α-Phyllohæmin and the Formula of α-Phylloporphyrin. LEON MARCHLEWSKI and J. ROBEL (*Ber.*, 1912, **45**, 816—821. Compare this vol., i, 288).—α-Phyllohæmin, obtained by the action of Mohr's salt on α-phylloporphyrin, can be purified by treatment with chloroform and quinine, and pouring the solution into glacial acetic acid saturated with common salt and heated nearly to boiling. After a time well-formed, brown, glistening, rhombic crystals are obtained, having a composition corresponding with either $C_{31}H_{34}O_2N_4FeCl$ or $C_{32}H_{34}O_2N_4FeCl$. The analytical figures obtained for phylloporphyrin itself make the formula $C_{32}H_{36}O_2N_4$ the most probable for this substance.

α-Phyllohæmin dissolves in organic solvents more easily than hæmin. In chloroform solution it has four absorption bands, which in comparison with those of hæmin are displaced somewhat towards the violet. In presence of quinine only two bands are visible.

α-Phyllohæmochromogen, obtained on reduction with Stokes' reagent, is very similar to hæmochromogen from hæmin. E. F. A.

Resorcinolbenzein and Fluorescein. HANS VON LIEBIG (*J. pr. Chem.*, 1912, [ii], **85**, 97—136, 241—284)—I. *Resorcinolbenzein.*—In continuation of previous work (Abstr., 1905, i, 781; 1906, i, 445; 1908, i, 98) the author has made a detailed examination of resorcinolbenzein obtained by the methods of Doebner (Abstr., 1883, 861) and Cohn (Abstr., 1893, i, 719; 1894, i, 120), and finds that it exists in four different forms.

The simplest form, α-resorcinolbenzein, has the composition $C_{19}H_{12}O_3$, and is identical with the resorcinolbenzein of Kehrmann and Dengler (Abstr., 1908, i, 1002; 1909, i, 249), whilst the β-, γ-, and δ-compounds are respectively ter-, quadri-, and multi-molecular modifications.

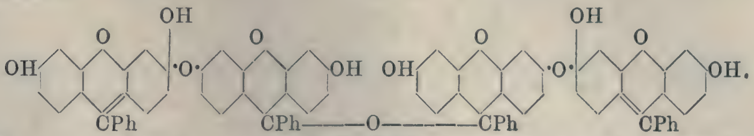
The product obtained by fusing benzoic acid or benzoic anhydride with resorcinol and zinc chloride at 180—210°, when treated with hot water and then with cold alcohol, yields a residue consisting of a *compound* of 2:4-dihydroxybenzophenone and γ-resorcinolbenzein, $2C_{19}H_{12}O_3,C_{13}H_{10}O_3,H_2O$, which forms light brown leaflets, m. p. 243—244°. On crystallisation from hot alcohol this yields a *substance*, m. p. 320—330°, having the same percentage composition, but crystallising in brownish-red, rhombic leaflets of a bluish lustre. Addition of acetic acid to an alcoholic solution of dihydroxybenzophenone-γ-resorcinolbenzein gives rise to the *compound*,

$$C_{19}H_{12}O_3,C_{13}H_{10}O_3,CH_3\cdot CO_2H,$$

which crystallises in brown leaflets of a silvery lustre, and is identical with the resorcinolbenzein of Cohn and Doebner.

γ-*Resorcinolbenzein* is obtained in brownish-red leaflets of the composition $4C_{19}H_{12}O_3,2H_2O,EtOH$, by dissolving the above-mentioned additive compound in alcoholic ammonia, and removing the excess of ammonia on the water-bath; it has also been prepared (1) by the oxidation of 3:6-dihydroxyphenylxanthen in alcoholic solution with lead dioxide in the presence of aqueous ammonia, and (2) by the action

of hydrogen peroxide on an ammoniacal solution of α- and β-resorcinolbenzein. It loses $1H_2O$ at 100° and, when dried at 140°, has the composition $4C_{19}H_{12}O_3,H_2O$; the remaining water is removed at 240°. It is considered by the author to be a quinhydrone of the following formula:



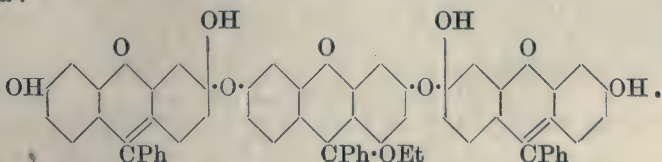
When treated with warm alcoholic hydrogen chloride and the resulting hydrochloride decomposed by ammonia, γ-resorcinolbenzein is converted into the α-compound. The main product obtained by heating benzotrichloride with resorcinol consists of a mixture of α-, β-, and γ-resorcinolbenzein; it is accompanied by small amounts of the following substances: (1) 2:4-Dihydroxybenzophenone. (2) The *compound*, $C_{19}H_{12}O_3,H_2O,C_{13}H_{10}O_3$, which forms a greenish-black powder, is resolved by boiling with alkalis and strong acids into dihydroxybenzophenone, and does not form salts. (3) *δ-Resorcinolbenzein*, $(C_{19}H_{14}O_4)_x$, a brownish-red, crystalline substance, insoluble in the common solvents with the exception of aniline and nitrobenzene; it is best prepared by fusing benzoic acid and resorcinol with zinc chloride at 250—260°.

The above-mentioned mixture of α-, β-, and γ-resorcinolbenzeins is sparingly soluble in alcohol, and is therefore readily separated from the remaining products of the reaction. On treatment with alcohol and hydrochloric acid, it yields a mixture of two hydrochlorides,

$$3C_{19}H_{12}O_3,3HCl,H_2O$$

and $C_{19}H_{12}O_3,HCl$ (compare Kehrmann and Dengler, *loc. cit.*), from which the corresponding bases are liberated by aqueous ammonia and separated by extraction with a mixture of alcohol and benzene.

α-Resorcinolbenzein, the more readily soluble base, crystallises in light red leaflets or needles of the composition $C_{19}H_{12}O_3,EtOH$; these lose their alcohol at 140—150°, and have m. p. 333°. The residue from the extraction consists of *β-resorcinolbenzein*, which separates from alcohol in red needles or leaflets of the composition $3C_{19}H_{12}O_3,3EtOH$; at 140° it loses two molecules of alcohol. The author considers that the third molecule of alcohol is combined in the form of an ether, and assigns to β-resorcinolbenzein the following formula:



When dissolved in alcoholic ammonia and the excess of the latter removed by boiling, the β-compound yields red leaflets of the composition $3C_{19}H_{12}O_3,H_2O,2EtOH$; at 140° these lose water and one molecule of alcohol, the second being removed at 240.°

The condensation of 2 : 4-dihydroxybenzophenone and resorcinol yields mainly β-resorcinolbenzein. The α-, β-, and γ-compounds when dissolved in aqueous ammonia and the solutions acidified with acetic acid yield crystalline *hydrates* of the same composition, $C_{19}H_{12}O_3,H_2O$.

Diacetylresorcinolbenzein (3 : 6-*diacetoxyphenylxanthanol*),

$$OH\cdot CPh<\begin{matrix}C_6H_3(OAc)\\C_6H_3(OAc)\end{matrix}>O,$$

crystallises in white leaflets, m. p. 171°, containing one molecule of ether which is lost at 140°. It dissolves in methyl alcohol, yielding the *methyl ether*, $OMe\cdot CPh<\begin{matrix}C_6H_3(OAc)\\C_6H_3(OAc)\end{matrix}>O$, white leaflets, m. p. 122°; the *ethyl ether* forms colourless prisms, m. p. 147°.

On treatment with acetic acid, acetic anhydride, and sulphuric acid, resorcinolbenzein yields a *monoacetyl* derivative,

$$CPh<\begin{matrix}C_6H_3(:O)—\\C_6H_3(OAc)\end{matrix}>O,$$

which crystallises in small, yellowish-red prisms, m. p. 197°, or in yellow needles containing benzene; in one instance an *acetyl* derivative of a dimolecular form, $C_{40}H_{28}O_8$, crystallising in colourless leaflets, m. p. 198°, was obtained. When methylated by means of methyl sulphate and aqueous sodium hydroxide, it forms the resorcinolbenzein monomethyl ether of Kehrmann and Dengler, together with an *anhydride* of *resorcinolbenzein dimethyl ether*, which crystallises from ether in colourless prisms, m. p. 152—153°, containing one molecule of the solvent, $(C_{21}H_{17}O_3)_2O,C_4H_{10}O$; the latter compound is converted by hot ethyl alcohol into the ethyl ether, m. p. 157°, described by Kehrmann; the corresponding methyl ether has m. p. 112°.

3 : 6-Dihydroxyphenylxanthen (Abstr., 1909, i, 98) separates from benzene in crystals of the composition $C_{19}H_{14}O_3,C_6H_6$; its ethereal solution on evaporation over benzene yields the *compound*,

$$2C_{19}H_{14}O_3,C_6H_6.$$

The compound, $C_{38}H_{30}O_9$, previously obtained (*loc. cit.*) by boiling resorcinol with aqueous potassium hydroxide is now found to consist of 2 : 4-dihydroxybenzophenone.

3 : 6-Diacetoxyphenylxanthen has m. p. 183—184°, and often separates from ethyl acetate in crystals, m. p. 179°, of the composition $4C_{19}H_{12}(OAc)_2,H_2O,CH_3\cdot CO_2Et$; crystallised from benzene, it has the composition $4C_{19}H_{12}(OAc)_2,C_6H_6$.

3 : 6-*Diacetoxyphenylxanthensulphonic acid*, $C_{23}H_{18}O_5\cdot SO_3H$, prepared by dissolving the preceding diacetoxy-compound in cold concentrated sulphuric acid, crystallises in white needles, and forms a *barium* salt.

Resorcinolbenzein forms with nitrobenzene the *compound*,

$$4C_{19}H_{12}O_3,3H_2O,C_6H_5\cdot NO_2,$$

crystallising in red needles, and with aniline the *compound*,

$$4C_{19}H_{12}O_3,C_6H_5\cdot NH_2,$$

dark red needles of a bluish lustre; the *compound* with phenol,

$$4C_{19}H_{12}O_3,H_2O,C_6H_5\cdot OH,$$

forms lustrous, light red needles.

The blue dye (resorcinol-blue) obtained by atmospheric oxidation of an ammoniacal resorcinol solution is more readily prepared by oxidising

the solution with hydrogen peroxide. It has the composition

$$C_6H_3(OH)_2\cdot N[C_6H_2(OH)_3]_2,$$

and m. p. above 360°; the filtrate on acidification with sulphuric acid yields a blue *compound*, $C_{18}H_{15}O_8N$. The successive addition of acetic acid and ammonium sulphate to an aqueous solution of resorcinol-blue gives rise to a mixture of the *compounds*, $C_{18}H_{15}O_8N,(NH_4)_2SO_4,H_2O$ and $C_{18}H_{15}O_8N,(NH_4)_2SO_4,NH_3$.

When oxidised with aqueous hydrogen peroxide, resorcinol yields a brown *dye* (*resorcinol-brown*), $C_{18}H_{14}O_8$.

II. *Fluorescein.*—In addition to the ordinary red variety, fluorescein exists in five different yellow modifications, distinguished by the author as α, β I, β II, γ and δ-fluorescein. The existence of these yellow modifications, all of which are unimolecular in acetone solution, is explained on the assumption that the three phenyl groups of triphenylmethane are not always freely moveable about the central atom, but, in certain circumstances, may take up different, fixed positions to one another. From molecular weight determinations in phenol solution, Kehrmann has drawn the conclusion that the red variety of fluorescein is also unimolecular. The author points out, however, that determinations in phenol solution give the molecular weight, not of the red form, but of the yellow modification, since on allowing the solution to solidify and removing the phenol with benzene or ether, yellow leaflets of a *compound* of fluorescein with phenol,

$$2C_{20}H_{12}O_5,C_6H_5\cdot OH,H_2O,$$

are obtained. It is suggested that the red form is a multimolecular quinhydrone of fluorescein.

α-Fluorescein, $C_{20}H_{12}O_5$, is obtained as a pale yellow powder, m. p. 347°, by acidifying an alkaline solution of ordinary fluorescein with sulphuric acid, extracting with ether, and shaking the ethereal solution with aqueous potassium hydroxide in insufficient amount for complete solution. It crystallises unchanged from benzene, amyl alcohol, and formic acid, but is converted by ethyl alcohol, acetone, ethyl acetate, and ether into the red form. From a mixture of methyl alcohol and ether, it separates in yellow crystals containing one molecule of methyl alcohol.

β-Fluorescein I is obtained by acidifying an aqueous solution of the disodium salt of fluorescein with sulphuric acid. It separates from ether in transparent, light yellow crystals, often in the form of hexagonal platelets, of the composition $4C_{20}H_{12}O_5,H_2O,4C_4H_{10}O$. It sinters and becomes brown at 140—150°, loss of ether taking place simultaneously; at 200° it loses water and becomes red. When dry, it is very stable, but in the moist condition and on exposure to light it is transformed into the red variety. It differs from the preceding modification in being stable in ethereal solution.

β-Fluorescein II, prepared by shaking an aqueous solution of the disodium salt of fluorescein with methyl sulphate, crystallises with ether in hexagonal platelets of the composition $C_{20}H_{12}O_5,C_4H_{10}O$; the ether is lost at 150—154°. It has about the same solubility as the β I modification, but differs from the latter in separating from acetone in yellow crystals containing one molecule of the solvent; it also crystallises with 1MeOH.

When heated at 220—240°, 2 : 4-dihydroxybenzoylbenzoic acid (m. p. 210—211°) yields two forms of fluorescein : (1) a red modification, which crystallises in lustrous, hexagonal leaflets, separates from methyl alcohol in yellow crystals of the composition $C_{20}H_{12}O_5$,MeOH, and differs in some respects from the ordinary red variety ; (2) *γ-fluorescein*, which forms a pale yellow, crystalline powder of the composition $4C_{20}H_{12}O_5,H_2O$, has approximately the same solubility as α-fluorescein, but differs from the latter in that it may be repeatedly crystallised from cold alcohol without undergoing change.

δ-Fluorescein is obtained together with a brown *substance*, $C_{40}H_{30}O_5$ (?), m. p. above 350°, by acidifying an aqueous solution of the mono- or di-sodium and potassium salts of fluorescein, which have been previously heated to 300—350°. It crystallises with one molecule of ether in crusts of transparent, yellow needles. From cold alcohol it separates in slender, chamois-coloured needles, which have the composition $C_{20}H_{12}O_5$, darken at 280—290°, and have m. p. 340°.

All the yellow forms of fluorescein give the same diacetyl derivative, m. p. 205—206° (Baeyer gives 200°) ; the *monoacetyl* derivative has m. p. 215°.

2 : 4 - Dihydroxybenzoylbenzoic acid crystallises from water in leaflets of the composition $2C_{14}H_{10}O_5,3H_2O$; the *diacetyl* derivative forms rhombohedra, m. p. 136°.

Fluorescin, prepared by reducing fluorescein with zinc dust and acetic acid in the presence of alcohol and aqueous ammonia, crystallises with $2H_2O$ in colourless or yellow leaflets, m. p. 253—254° (compare Herzig, Abstr., 1892, 1319). It crystallises with ether in needles, and with benzene (2 mols.) in leaflets ; the *diacetyl* derivative has m. p. 213—214°, and forms crystals containing alcohol, m. p. 113—114°.

III. *Alkali Salts of the Fluorescein Series.*—This section contains an account of the preparation of the sodium and potassium salts of fluorescein, and of some allied compounds, together with a discussion of their constitution.

The *monopotassium* salt of fluorescein, $C_{20}H_{11}O_5K$, prepared from fluorescein or its diacetyl derivative and alcoholic potassium hydroxide, crystallises with alcohol (1 mol.) in orange or light red needles, and is almost instantly decomposed by water with the separation of fluorescein ; the *ammonium* salt, $C_{20}H_{15}O_5N$,EtOH, forms lustrous, red leaflets. The *dipotassium* salt, $C_{20}H_{10}O_5K_2,3H_2O$, obtained as a greenish-black mass of a bluish lustre, gives light red solutions which become dark red on the addition of a trace of alkali ; this change is referred by the author to the rupture of the oxygen bridge of the central ring ; the *disodium* salt is similar in character.

The *potassium* salt of fluoran, $C_{20}H_{13}O_4K$,EtOH, forms long, colourless needles. When methylated by means of methyl sulphate and aqueous potassium hydroxide, quinolphthalein yields a *dimethyl ether*, $2C_{20}H_{10}O_3(OMe)_2,H_2O$, which crystallises in bluish leaflets, m. p. 198°, and yields a colourless *potassium* salt, $C_{44}H_{17}O_4(OMe)_4K_3$. The *sodium* and *potassium* salts of resorcinolbenzein, $C_{19}H_{11}O_3$Na(or K), crystallise in light, red needles or leaflets ; the *dipotassium* salt of quinolphthalein, $C_{20}H_{10}O_5K_2,3H_2O$, is bluish-black.

IV. *The Methyl Ethers of Fluorescein.*—The author discusses the

constitution of the methyl ethers of fluorescein, and gives an account of the products obtained by methylating fluorescein under different conditions. The monomethyl ether described by Fischer (Abstr., 1895, i, 291) has m. p. 266°; it is pale yellow in colour, and has the constitution $O{<}{}^{C_6H_3(OMe)}_{C_6H_3O}{>}C{\cdot}C_6H_4{\cdot}CO_2H$. The interaction of methyl sulphate and the disodium salt of fluorescein yields, in addition to the above compound, the previously-described dimethyl ethers of m. p. 198° and 208°, together with a new *dimethyl ether*, which crystallises in small, colourless prisms, m. p. 255°; the properties of the latter compound are in agreement with the formula:

$$O{<}{}^{C_6H_3(OMe)}_{C_6H_3(OMe)}{>}C{<}{}^{O}_{C_6H_4}{>}CO,$$

which, however, has already been assigned to the dimethyl ether of m. p. 198°.

On treatment with methyl iodide in methyl-alcoholic solution, the disodium salt of fluorescein yields a bimolecular *methyl ether*,

$$C_{21}H_{14}O_5,C_{22}H_{16}O_5,H_2O,$$

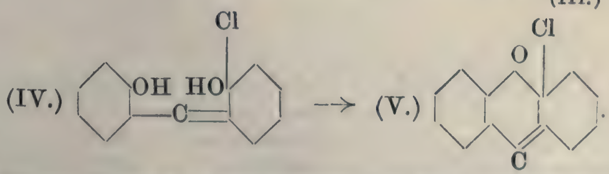
crystallising in slender, orange-yellow needles, m. p. 164—165° (decomp.).

When fluorescein is methylated according to Fischer's method (Abstr., 1895, i, 291) and the product of the action extracted with ether, a *hydrate* of the dimethyl ether, m. p. 208°, is obtained; this crystallises in orange-yellow needles, sintering at 173—174°, and has the composition $3C_{22}H_{16}O_5,2H_2O$. Extraction with cold methyl alcohol yields a *hydrate*, $2C_{22}H_{16}O_5,H_2O$, light yellow needles, m. p. 190°, whilst the hot methyl-alcoholic extract furnishes a *hydrate*, $3C_{22}H_{16}O_5,H_2O$, crystallising in orange-yellow needles, which often pass spontaneously into dark red prisms, m. p. 194°. All three hydrates when heated at 140°, or repeatedly crystallised from ethyl acetate, yield the anhydrous dimethyl ether, m. p. 208°.

V. *Quinhydrones and Oxonium Salts.*—In this section the author advances arguments in favour of the view that the compounds of resorcinolbenzein and fluorescein with dihydroxybenzophenone and alcohol described in sections I and II, and also the oxonium salts of the xanthen series have a quinhydrone structure. The formation of oxonium salts is due to the rupture of the oxygen bridge and intermediate formation of an *o*-quinonoid compound (III), as shown in the following scheme:

$$C_6H_4{<}{}^{O}_{C}{>}C_6H_4 \longrightarrow C_6H_4{<}{}^{OH\ \ HO}_{\ \ C\ \ }{>}C_6H_4 \longrightarrow C_6H_4{<}{}^{OH\ \ O}_{\ \ C\ \ }{\geqslant}C_6H_4$$

(III.)



In the solid condition the salts are represented by formula (V) and in solution by (IV).

a-Resorcinolbenzein chloride, $C_{19}H_{12}O_3,HCl$, prepared by the action of alcoholic hydrogen chloride on a-resorcinolbenzein, forms light yellow needles or leaflets. *β-Resorcinolbenzein chloride*,

$$3C_{19}H_{12}O_3,3HCl,EtOH,$$

crystallises in brownish-yellow needles or leaflets. γ-Resorcinolbenzein and alcoholic hydrogen chloride yield either the above a-chloride or *γ-resorcinolbenzein chloride*, $4C_{19}H_{12}O_3,4HCl,H_2O$, which forms steel-blue, rhombic, broad leaflets.

On treatment with a mixture of sulphuric and acetic acids, resorcinolbenzein forms a *sulphate*, $(C_{19}H_{12}O_3)SO_4$, crystallising in yellow needles of a violet lustre. When boiled with 25% sulphuric acid, it forms a *sulphate*, $C_{19}H_{12}O_4,H_2SO_4$; this crystallises in yellow leaflets, which are transformed by water into lustrous, red needles of the composition $4C_{19}H_{12}O_3,2H_2SO_4,2H_2O$. When treated successively with acetic anhydride and sulphuric acid, and the resulting product dissolved in aqueous ammonia, resorcinolbenzein yields an *ammonium* salt of the monoacetyl derivative of resorcinolbenzein sulphate,

$$C_{19}H_{11}O_2\cdot OAc,H_2O,H_2SO_4,NH_3,$$

which forms glistening, red needles.

The *chloride* of *resorcinolbenzein dimethyl ether*,

$$C_{21}H_{18}O_4,H_2O,2HCl,$$

crystallises in long, slender, yellow needles, the *sulphate* in yellow leaflets.

When boiled with glacial acetic acid, the ordinary red fluorescein yields a red *acetate*, $4C_{20}H_{12}O_5,CH_3\cdot CO_2H$; the yellow varieties of fluorescein yield a golden-yellow *acetate*, $C_{20}H_{12}O_5,CH_3\cdot CO_2H$, which crystallises in leaflets of a green lustre.

With alcoholic hydrogen chloride, fluorescein gives a *chloride*,

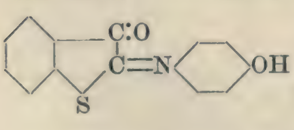
$$4C_{20}H_{12}O_5,4HCl,4EtOH,H_2O,$$

crystallising in yellow, hexagonal leaflets of a green lustre (decomp. 270°); the *sulphate*, $2C_{20}H_{12}O_5,H_2SO_4$, is also described.

The dimethyl ether of fluorescein of m. p. 198° forms a yellow *chloride* of the composition $3C_{22}H_{16}O_5,2HCl$.

When boiled with 2% hydrochloric acid the dimethyl ether of m. p. 208° yields a termolecular *chloride*, $3C_{22}H_{16}O_5,2HCl,4H_2O$, crystallising in red needles (decomp. 120°); with alcoholic hydrogen chloride it forms a unimolecular *chloride*, $C_{22}H_{16}O_5,HCl,2H_2O$, which crystallises in large, dark red prisms of a blue lustre (decomp. 120°). F. B.

Preparation of *p*-Hydroxyaryl Derivatives of 2-Imino-3-ketodihydro-(1)-thionaphthens. KALLE & Co. (D.R.-P. 241623).—When a-(2)-derivatives of 2 : 3-diketodihydro-(1)-thionaphthens are oxidised in the presence of hydroxyarylamines in alkaline solution, condensation products are produced.



The *compound* (annexed formula), yellow needles, was obtained by the action of potassium ferricyanide on a mixture of *p*-aminophenol and 3-keto-(1)-thionaphthen-2-carboxylic acid in aqueous alkaline solution. The *sodium* salt is soluble in water with violet

coloration, and when boiled with 20% sulphuric acid furnishes 2 : 3-diketodihydro-(1)-thionaphthen. F. M. G. M.

***apo*Harminecarboxylic Acid, *apo*Harmine, and Some Derivatives of this Base.** VICTOR HASENFRATZ (*Compt. rend.*, 1912, **154**, 704—706. Compare this vol., i, 209).—*apo*Harminecarboxylic acid may be obtained directly from harmic acid by heating it at 250—280° in a vacuum. A second molecule of carbon dioxide is lost at 330°, and *apo*harmine is formed; harmic acid, therefore, appears to be *apo*harmine-2 : 3-dicarboxylic acid.

*Iodo*apo*harmine*, $C_8H_7N_2I$, prepared by the action of iodine on *apo*harmine in presence of potassium hydroxide, occurs in long needles, m. p. 158°; the *platinichloride* and *nitrate* were prepared, the latter crystallises with $1H_2O$. By the action of methyl iodide, *iodomethyl*apo*harmine hydriodide* is obtained; the *base*, $C_8H_6MeN_2I$, crystallises in needles, m. p. 155—156°.

apo*Harminesulphonic acid*, $C_8H_7N_2{\cdot}SO_3H$, crystallising in colourless prisms, is formed when *apo*harmine dissolves in sulphuric acid. Harmaline likewise yields *harmalinesulphonic acid*, $C_{13}H_{13}ON_2{\cdot}SO_3H$, in the form of long, golden-yellow needles, which give an intensely fluorescent, blue solution in water. W. O. W.

Resolution of Racemic Histidine into the Optically Active Components. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, **77**, 435—453).—Natural *l*-histidine has been racemised by heating under pressure, and this resolved into *d*- and *l*-histidines by means of *d*-tartaric acid (compare Pyman, Trans., 1911, **99**, 1386).

Formyl-*l*-histidine has $[\alpha]_D^{20}$ +56·73°. Formyl-*dl*-histidine could not be resolved by means of brucine. *dl*-Histidine is partly resolved by yeast, *d*-histidine remaining unattacked. Pure *d*-histidine was obtained from the urine of rabbits fed with *dl*-histidine. E. F. A.

Preparation of Hydrastinine and Analogous Bases from Berberine. MARTIN FREUND (D.R.-P. 241136).—A general method for the preparation of hydrastine bases consists of the following procedure. The *a*-alkyl-, *a*-alkaryl-, or *a*-aryl-dihydroberberines are reduced to the tetrahydro-condition (I), converted into the quaternary compound (II), and finally into the ammonium base (III) and the pseudo-base, for which several formulæ may be given; further elimination of water may take place, yielding a complicated series of compounds, or the base may be converted by oxidation into hydrastinine derivatives.

(I) $C_{20}H_{18}RO_4N + H_2 = C_{20}H_{20}RO_4N$.
(II) $C_{20}H_{20}RO_4N + MeI = C_{20}H_{20}RO_4NMeI$.
(III) $C_{20}H_{20}RO_4NMe{\cdot}OH = H_2O + C_{20}H_{19}RO_4NMe$.

a-Benzyltetrahydroberberine, greenish-yellow needles, m. p. 163—165°, is prepared by reducing benzyldihydroberberine with tin and alcoholic hydrochloric acid; the *stannichloride* which crystallises out is decomposed with ammonium sulphide, and the free base extracted with chloroform. *Tetrahydroberberine methiodide* is obtained by heating the foregoing base with methyl iodide at 225° during four or five hours;

this when digested with silver hydroxide in 50% alcoholic solution furnishes a crystalline *base*, m. p. 121—122°, which when oxidised with sodium dichromate in 50% acetic acid solution furnishes a 65—78% yield of hydrastinine. F. M. G. M.

Action of Sodium Ethoxide on Pyrrole Derivatives. I. HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1912, **77**, 185—201).—By reduction of the hydrazone of 3-acetyl-2 : 4-dimethylpyrrole with sodium ethoxide, Knorr and Hess (Abstr., 1911, i, 1019) obtained 2 : 4-dimethyl-3-ethylpyrrole,

$$NH<\begin{matrix}CH{=}CMe\\ CMe{:}CEt\end{matrix}$$

On repetition of this operation, a ketazine is obtained instead of the hydrazone, which, when reduced at 220°, affords an oil differing greatly in properties from that obtained by Knorr and Hess. The new oil does not immediately form a picrate with picric acid or yield methylethylmaleinimide when treated with lead peroxide. It is characterised by the formation of a crystalline azo-dye with diazobenzenesulphonic acid. An azo-dye of similar properties is obtained from Piloty's phonopyrrole.

On immediate addition of picric acid to the ethereal solution of the freshly distilled oil, a *picrate*, m. p. 89—90°, was obtained, corresponding with a dimethyldiethylpyrrole. The free pyrrole was not obtained crystalline; it does not couple with diazobenzenesulphonic acid.

2 : 4-Dimethyl-5-ethylpyrrole, $NH<\begin{matrix}CEt{=}CMe\\ CMe{:}CH\end{matrix}$, was obtained synthetically from ethyl acetoacetate and methyl propyl ketoxime. By means of the azo-dye compound it is shown to be identical with the above oil obtained from the ketazine. By the action of sodium ethoxide at 220°, 2 : 4-*dimethyl*-3 : 5-*diethylpyrrole*, $NH<\begin{matrix}CEt{=}CMe\\ CMe{:}CEt\end{matrix}$, identical with that derived from the picrate, is obtained.

3-*Acetyl*-2 : 4 : 5-*trimethylpyrrole*, $NH<\begin{matrix}CMe{:}CMe\\ CMe{:}C{\cdot}COMe\end{matrix}$, from methyl ethyl ketoxime and acetylacetone, has m. p. 209°; it does not couple with diazobenzenesulphonic acid. By the action of hydrazine-hydrate, a mixture of ketazine and hydrazone, m. p. 235—236°, is obtained; when this is heated with sodium ethoxide at 220°, 2 : 4 : 5-trimethyl-3-ethylpyrrole is obtained, m. p. 65—67°, which forms a picrate, m. p. 104—105°, identical with phyllopyrrole picrate. E. F. A.

Electrolytic Reduction of Chelidamic Acid to 4-Hydroxy-piperidine-2 : 6-dicarboxylic Acid. BRUNO EMMERT and AUGUST HERTERICH (*Ber.*, 1912, **45**, 661—665).—The cathodic and the anodic compartments of Tafel's apparatus contain respectively chelidamic acid in *N*-sodium hydroxide and 10% sodium carbonate. The reduction is effected at 25—30° at a lead cathode, the current density being 11

amperes per sq. decimetre. 4-*Hydroxypiperidine*-2 : 6- *icarboxylic, acid*, $C_7H_{11}O_5N$, decomp. above 240°, crystallises in short prisms, rapidly absorbs moisture from the air, and forms a *hydrochloride* decomp. 230°. It can be esterified only with difficulty. The *ethyl* ester has b. p. 206—208°/15 mm. (*hydrochloride*, decomp. 195°); the *methyl* ester has b. p. 185—187°/15 mm.; the *diamide* has m. p. 245° (decomp.). C. S.

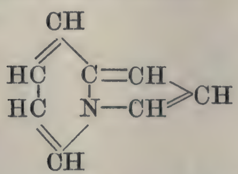
Action of Acetic Anhydride on α-Picoline. MAX SCHOLTZ (*Ber.*, 1912, 45, 734—747).—When α-picoline is treated with acetic anhydride at 200—220°, interaction occurs according to the equation: $C_6H_7N + 2(CH_3{\cdot}CO)_2O = C_{12}H_{11}O_2N + CH_3{\cdot}CO_2H + 2H_2O$.

The compound, $C_{12}H_{11}O_2N$, possessed no basic properties, and hence probably does not contain the pyridine ring. This is confirmed by the fact that no pyridinecarboxylic acid could be obtained by oxidising it. With hydroxylamine, phenylhydrazine, and semicarbazide it forms crystalline condensation products. It readily condenses with two molecules of aromatic aldehydes, whilst, in some cases, monoaldehyde compounds can also be isolated. It therefore contains the group $\cdot CH_2{\cdot}CO{\cdot}CH_2\cdot$ or, more probably, $\cdot CH_2{\cdot}CO{\cdot}CH_3$. It combines with two or four atoms of bromine, yielding very unstable products. When boiled with moderately concentrated sulphuric or hydrochloric acid, it yields a base, C_8H_7N, isomeric with indole. For the substance, $C_{12}H_{11}O_2N$, which probably possesses the formula

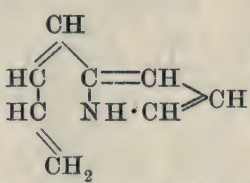
$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_8H_3{:}N{\cdot}CO{\cdot}CH_3,$$

the name *picolide* is proposed.

The compound, C_8H_7N, is a very weak base, from which crystalline salts could not be obtained. It does not react with methyl iodide at 100°. It is very readily oxidised. It gives the pyrrole reaction with isatin and with a pine shaving, whilst with oxalic acid it gives the indole reaction. When reduced, it yields a compound, C_8H_9N, which is not basic, but behaves as a pyrrole derivative. For these two compounds the formulæ:



and



are proposed, and the former is named *pyrrocoline*. Both it and its dihydro-derivative form crystalline compounds with aldehydes, in which two molecules of the pyrrole derivative unite with one molecule of aldehyde.

2 : 4-Lutidine, when treated with acetic anhydride, yields methylpicolide, $C_{13}H_{13}O_2N$.

Picolide, $C_{12}H_{11}O_2N$, is best obtained by heating α-picoline at 200—220° with a large excess of acetic anhydride and boiling the product with much water. On cooling, picolide separates in long needles, m. p. 176°. Its formation can be used to detect the presence

of 2-picoline in commercial pyridine. It yields an *oxime*, m. p. 244°, a *phenylhydrazone*, m. p. 168°, and a *semicarbazone*, m. p. 233°. By treating its alcoholic solution with aromatic aldehydes, the following condensation products were obtained: *dibenzylidenepicolide*, m. p. 208°; *di*-p-*methylbenzylidenepicolide*, m. p. 202°; *mono*-p-*methylbenzylidenepicolide*, m. p. 152°; *difurfurylidenepicolide*, m. p. 210°; *dicinnamylidenepicolide*, m. p. 217°; *di*-p-iso*propylbenzylidenepicolide*, m. p. 214°; *dipiperonylidenepicolide*, m. p. 141°, and *piperonylidenepicolide*, m. p. 152°. These aldehyde condensation products give characteristic colorations on treatment with concentrated sulphuric acid.

Pyrrocoline, C_8H_7N, obtained by boiling picolide during an hour with 25% hydrochloric acid and purified by distillation with steam, has m. p. 74°, b. p. 205°. When dissolved in very dilute sulphuric acid and treated with potassium iodate, it gives an intensely blue solution. When condensed with aldehydes, it yields the following compounds, which are somewhat sensitive to the action of air: *benzylidenedipyrrocoline*, m. p. 210—212°; p-*methylbenzylidenedipyrrocoline*, m. p. 92°; *cinnamylidenedipyrrocoline*, darkening above 200°; *furfurylidenedipyrrocoline*, m. p. 148—149°; *piperonylidenedipyrrocoline*, m. p. 145—150°; *chloralpyrrocoline*, $CCl_3\cdot CH(OH)\cdot C_8H_6N$, m. p. 92°.

Dihydropyrrocoline (*2-butadienylpyrrole*), C_8H_9N, obtained by reducing pyrrocoline by sodium and alcohol, is a colourless oil, b. p. 198—199°/754 mm. When dissolved in alcohol and treated with an alcoholic solution of mercuric chloride, it yields a *compound*, $C_8H_9NCl_4Hg_2$, decomposing above 90°. When warmed with the respective aldehydes, dihydropyrrocoline yields *benzylidene-bis-dihydropyrrocoline*, m. p. 118—120°, and *furfurylidene-bis-dihydropyrrocoline*, m. p. 132°.

Methylpicolide, m. p. 180°, is obtained in small yield by heating 2 : 4-lutidine with acetic anhydride. H. W.

New Metallo-quinolides. Metallo-quinolides of Silver Nitrate. I. UMBERTO POMILIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 326—341).—When quinoline and silver nitrate are brought together in aqueous solution or in the solid state, the compound, $AgNO_3(C_9H_7N)_2$, is produced (compare Lachowicz, Abstr., 1890, 444). When a solution of silver nitrate in excess of quinoline is heated for some hours at 30—35°, the crystalline compound, $AgNO_3(C_9C_7N)_4$ is obtained on cooling. This substance readily loses quinoline when treated with solvents, the diquinolide being formed.

R. V. S.

New Metallo-quinolides. Metallo-quinolides of Nickel Chloride. II. UMBERTO POMILIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 342—352).—Quinoline and well-dried, anhydrous nickel chloride were left in contact for some weeks, then heated at 100° for a few days, and finally kept at 200° for some hours. The liquid, after being filtered while warm, deposited a dark blue, crystalline *compound*, $NiCl_2(C_9H_7N)_2$. When the reaction mixture was cooled rapidly, a

yellow *compound* of the same composition was obtained mixed with the blue substance. A mixture of the two substances kept in a sealed tube was entirely converted into the yellow compound in a few hours, and the two substances are therefore to be regarded as isomerides or polymerides. When the blue compound is heated at 140—150°, and finally at 160—170°, or when the yellow salt is heated at 120—130° and subsequently at 150—170°, the red *compound*, $NiCl_2,C_9H_7N$, is produced. All three substances are readily decomposed by solvents (especially alcohol), and this may explain the failure to obtain such compounds previously (compare Lachowicz, Abstr., 1889, 569).

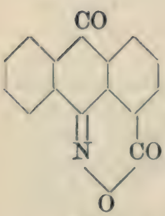
Anhydrous nickel sulphate and quinoline, kept at 100° for some days, yield a stable *compound*, which forms a violet, crystalline crust, m. p. 98—99°. R. V. S.

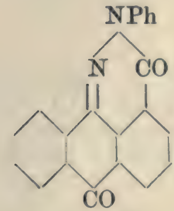
Anthraquinone Series. VII. Anthraquinone-1-carboxylic Acid. FRITZ ULLMANN and WILLEM VAN DER SCHALK (*Annalen*, 1912, **388**, 199—216).—Anthraquinone-1-carboxylic acid is easily obtained in 70% yield by the following series of reactions. Anthraquinone is nitrated at 50° by nitric (D 1·4) and sulphuric acids. The 1-nitroanthraquinone (separated from the little dinitroanthraquinone produced by solution in toluene) is reduced by sodium sulphide and boiling water to 1-aminoanthraquinone. This is diazotised and the separated diazonium sulphate is treated in the usual manner with cuprous cyanide at 70°, and the resulting nitrile is hydrolysed by boiling dilute sulphuric acid (3 : 1 by volume). The acid is purified by solution in aqueous ammonia and precipitation by dilute nitric acid.

In a similar manner 2-bromo-1-aminoanthraquinone is converted into 2-*bromo*-1-*cyanoanthraquinone*, m. p. 308° (corr.), and 2-*bromoanthraquinone*-1-*carboxylic acid*, m. p. 292° (corr.), yellow octahedra. 5-*Nitroanthraquinone*-1-*carboxylic acid*, decomp. above 330°, yellow plates, is obtained by the nitration of the acid or by converting 5-nitro-1-aminoanthraquinone into the *nitrile*, m. p. 390°, and subsequent hydrolysis. By reduction with boiling aqueous sodium sulphide, it yields 5-*aminoanthraquinone*-1-*carboxylic acid*, m. p. 277° (decomp.), dark red leaflets.

Oxazonanthrone (*anhydro-anthraquinone*-9-*oxime*-1-*carboxylic acid*), m. p. 247° (corr.), almost colourless needles, is obtained from anthraquinone-1-carboxylic acid and hydroxylamine in boiling aqueous solution, and receives the formula (1). It is soluble in boiling alkalis, and is reprecipitated by acids. The analogously constituted *pyridazonanthrone*, $C_{15}H_8O_2N_2$, m. p. 430°, almost colourless needles, is obtained by the slow addition of aqueous hydrazine hydrate to a pyridine solution of ethyl anthraquinone-1-carboxylate or to a benzene solution of the acid chloride. Anthraquinone-1-carboxylic acid and potassium acetate react with phenylhydrazine in boiling 50% acetic acid to form *phenylpyridazonanthrone* (formula II), m. p. 292° (corr.), yellow needles, by the sulphonation of which *phenylpyridazonanthrone*-p-*sulphonic acid*, yellow needles, is produced. This acid, which is also

obtained from anthraquinone-1-carboxylic acid and phenylhydrazine-*p*-sulphonic acid, forms a *sodium* salt, $C_{21}H_{11}O_5N_2SNa$, yellow, felted needles, which dyes wool in yellow shades fast to light and washing. 5-Aminoanthraquinone-1-carboxylic acid and phenylhydrazine in 50% acetic acid containing potassium acetate yield 5-*amino*-N-*phenylpyridazonanthrone*, $C_{21}H_{13}O_2N_3$, m. p. 320°, carmine-red leaflets, which develops a violet coloration in warm, concentrated sulphuric acid. N-*a*-*Anthraquinonylpyridazonanthrone*, m. p. 339°, yellow needles


(I.)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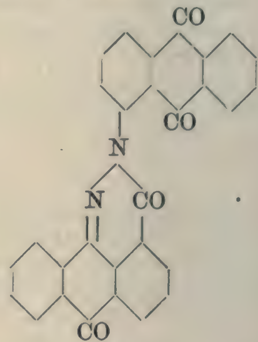
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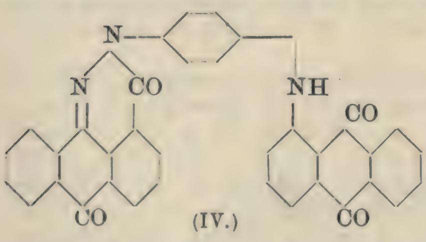
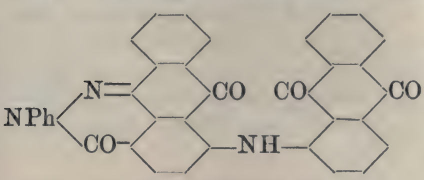
(formula III), is prepared by boiling pyridazonanthrone, *a*-chloroanthraquinone, copper powder, and potassium and copper acetates in nitrobenzene for ten hours. It is reduced by alkaline sodium hyposulphite to a brownish-red vat, which has only a slight affinity for cotton. When treated in a similar manner, p - *bromophenylpyridazon* - *anthrone*, $C_{21}H_{11}O_2N_2Br$, m. p. 308° (corr.), yellow needles (prepared from anthraquinone-1-carboxylic acid and *p*-bromophenylhydrazine), and 1-aminoanthraquinone yield *a*-*anthraquinonyl*-p-*aminophenylpyridazonanthrone* (formula IV), brownish-red needles, which reduces to a red vat dyeing cotton in weak red shades. C. S.


(IV.)

Anthraquinone Series. VIII. 4-Chloroanthraquinone-1-carboxylic Acid. FRITZ ULLMANN and WASSILY MINAJEFF (*Annalen*, 1912, **388**, 217—221).—4-Chloroanthraquinone-1-carboxylic acid, obtained by the oxidation of 4-chloro-1-methylanthraquinone by 100% sulphuric acid at 120°, is converted by hydrazine hydrate (compare preceding abstract) into 4-*chloropyridazonanthrone*, $C_{15}H_7O_2N_2Cl$, m. p. 319° (corr.), yellow needles, which reacts with boiling *p*-toluidine and potassium and copper acetates to form 4-p-*toluidinopyridazonanthrone*, $C_{22}H_{15}O_2N_3$, m. p. 352° (corr.), orange-red needles. 4-*Chloro*-N-*phenylpyridazonanthrone*, $C_{21}H_{11}O_2N_2Cl$, m. p. 285° (corr.), yellow needles, prepared from 4-chloroanthraquinone-1-carboxylic acid and phenyl-

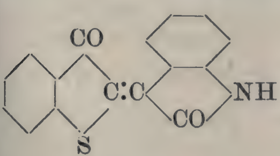
hydrazine (*loc. cit.*), reacts readily with *p*-toluenesulphonamide and potassium and copper acetates in boiling nitrobenzene to form 4-p-*toluenesulphonamino*-N-*phenylpyridazonanthrone*, which is converted by concentrated sulphuric acid on the water-bath into 4-*amino*-N-*phenylpyridazonanthrone*, m. p. 340° (corr.), yellow needles.

4-α-*Anthraquinonylamino*-N-*phenylpyridazonanthrone* (annexed formula), m. p. 405°, red needles, is prepared from 4-chloro-*N*-phenylpyridazonanthrone, 1-aminoanthraquinone, and potassium and copper acetates in boiling nitrobenzene.

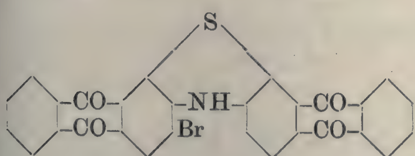


4-β-*Anthraquinonylamino*-N-*phenylpyridazonanthrone*, m. p. 430°, brown needles, is prepared in a similar manner from 2-aminoanthraquinone; unlike the α-isomeride, it yields a vat with sodium hyposulphite, and produces yellowish-brown shades on cotton. C. S.

[Preparation of Oxindole Derivatives of 2:3-Diketodihydro-1-thionaphthen.] KALLE & Co. (D.R.-P. 241327).—The *compound* (annexed formula), a brown, crystalline powder, was obtained by boiling oxindole and 2:3-diketodihydro-(1)-thionaphthen together in acetic acid solution in the presence of zinc chloride until the formation of colour was complete. The 2:3-diketodihydro-(1)-thionaphthen can be replaced by its derivatives substituted in the ring. F. M. G. M.



Thiodiphenylamines of the Anthraquinone Group. IRMA ULLMANN and FRITZ ULLMANN (*Ber.*, 1912, 45, 832—834. Compare Abstr., 1911, i, 466, 489, 739, 1010).—In extension of the earlier investigations it was desired to prepare compounds in which the carbonyl group of the anthraquinoneacridones is replaced by a sulphur atom.



Bromodianthraquinoylthiodiphenylamine (annexed formula) was obtained by interaction of 1:3-dibromo-2-aminoanthraquinone with anthraquinone-1-thiol in hot nitrobenzene solution in the presence of potassium hydroxide; it forms violet needle crystals, which sublime without melting (decomp.) above 400° Its solutions in organic solvents are violet, and it can be reduced to a brownish-red vat which dyes cotton violet-blue. D. F. T.

Sulphazone Dyes. MAX CLAASS (*Ber.*, 1912, 45, 747—756).—o-*Nitrophenylthiolacetic acid*, $NO_2\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$, m. p. 163—164°, yellowish-brown, slender needles, obtained from *o*-nitrophenyl mercaptan and chloroacetic acid in warm alkaline solution, is converted into o-*nitrophenylthionylacetic acid*, $NO_2\cdot C_6H_4\cdot SO\cdot CH_2\cdot CO_2H$, decomp.,

185—186°, by 3% hydrogen peroxide, and into o-*nitrophenylsulphone-acetic acid*, $NO_2\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot CO_2H$, m. p. 173—174°, colourless prisms, by 40% hydrogen peroxide. The latter is reduced by zinc dust and hot 50% acetic acid to *sulphazone*, $C_6H_4<\begin{matrix}NH\cdot CO\\ SO_2\cdot CH_2\end{matrix}$, m. p. 207—208°, brown leaflets, which is insoluble in sodium carbonate, dissolves in sodium hydroxide, and does not give a coloration with ferric chloride. The hydrogen atoms in the group $\cdot SO_2\cdot CH_2\cdot CO$ are very reactive. The present paper deals with the sulphazone dyes obtained by condensing sulphazone with diazonium salts in alkaline solution. Thus diazotised, α-naphthylamine-5-sulphonic acid yields 5-*sulphonaphthalene*-1(2′)-*azosulphazone*,

$$C_6H_4<\begin{matrix}NH\cdot C(OH)\\ SO_2\text{———}\end{matrix}>C\cdot N_2\cdot C_{10}H_6\cdot SO_3H,$$

in the form of its *sodium* salt, a dark brown powder, which dyes wool yellow or brownish-yellow, and silk golden-yellow. Diazotised 8-hydroxy-β-naphthylamine-6-sulphonic acid yields the *sodium* salt of 8-hydroxy-6-sulphonaphthalene-2(2′)-azosulphazone,

$$C_6H_4<\begin{matrix}NH\cdot C(OH)\\ SO_2\text{———}\end{matrix}>C\cdot N_2\cdot C_{10}H_5(OH)\cdot SO_3H,$$

a brown powder, which dyes wool yellowish-brown, and cotton violet-brown substantively. *Sulphazone*-1-*azodiphenyl*-4′-*azosalicylic acid*,

$$C_6H_4<\begin{matrix}NH\cdot C(OH)\\ SO_2\text{———}\end{matrix}>C\cdot N_2\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H,$$

obtained by condensing tetrazotised benzidine with sulphazone and salicylic acid in alkaline solution, is a dark brown, substantive dye, which produces a brilliant golden-orange shade on cotton. The *sodium* salt of p-*sulphobenzeneazo*-3-*sulphobenzene*-4-*azosulphazone*,

$$C_6H_4<\begin{matrix}NH\cdot C(OH)\\ SO_2\text{———}\end{matrix}>C\cdot N_2\cdot C_6H_3(SO_3Na)\cdot N_2\cdot C_6H_4\cdot SO_3Na,$$

obtained by condensing diazotised sulphanilic acid with sodium *o*-aminobenzenesulphonate, diazotising the product, and condensing it with sulphazone, is a reddish-brown powder, which dyes wool and silk a fine reddish-orange.

By reactions similar to the preceding, 2 : 4-dinitrophenyl mercaptan has been converted successively into 2 : 4-*dinitrophenylthiolacetic acid*, $C_6H_3(NO_2)_2\cdot S\cdot CH_2\cdot CO_2H$, m. p. 160°, yellowish-brown needles, and 2 : 4-*dinitrophenylsulphoneacetic acid*, $C_6H_3(NO_2)_2\cdot SO_2\cdot CH_2\cdot CO_2H$, which has not been obtained pure, but forms a *lead* salt, yellow needles, and readily loses carbon dioxide, yielding 2 : 4-*dinitrophenylmethylsulphone*, m. p. 185°. The reduction of the lead salt by tin and hydrochloric acid yields 6-*aminosulphazone*, $NH_2\cdot C_6H_3<\begin{matrix}NH\cdot C\cdot OH\\ SO_2\cdot CH\end{matrix}$, decomp. 280° (*hydrochloride*, brown prisms), which can be easily diazotised and subsequently condensed with amines or phenols, yielding dyes of very varying colour. C. S.

Hydantoins. IX. Action of Potassium Thiocyanate on Alanine. TREAT B. JOHNSON (*J. Biol. Chem.*, 1912, **11**, 97—101. Compare Johnson and Nicolet, this vol., i, 53; Komatsu, Abstr., 1911, i, 683).—Alanine reacts smoothly with potassium thiocyanate in

the presence of acetic anhydride, forming *2-thiol-3-acetyl-4-methylhydantoin*, $CS<\begin{matrix}NH-CO\\NAc\cdot CHMe\end{matrix}$; no evidence of the formation of a thiohydantoic acid as described by Komatsu (*loc. cit.*) was obtained. The same acetylthiolhydantoin was formed from acetylalanine; on digestion with hydrochloric acid it is converted quantitatively into 2-thiol-4-methylhydantoin (Wheeler, Nicolet, and Johnson, Abstr., 1911, i, 1031). Like the thiopolypeptides, the new thiolhydantoin contains the thioamide group, $-CS\cdot NH-$, which is probably active in the natural synthesis of sulphur proteins from simpler substances. *2-Thiol-3-acetyl-4-methylhydantoin* crystallises in stout prisms, m. p. 166°.

E. F. A.

Derivatives of Piperazine. ANTOINE P. N. FRANCHIMONT and E. KRAMER (*Rev. trav. chim.*, 1912, **31**, 40—75. Compare Abstr., 1907, i, 395; 1909, i, 327; 1910, i, 139).—An amplification of a previous paper (compare Abstr., 1910, i, 139). Piperazinediacetonitrile, like the corresponding amide, gives a *compound*,

$$C_8H_{12}N_4,2HCl,$$

with hydrochloric acid, which decomposes above 200°. Methyl piperazinediacetate monomethiodide, when shaken with silver hydroxide in methyl alcohol, gives a betaine *compound*, m. p. 235°, to which the formula $CO<\begin{matrix}CH_2\\-O-\end{matrix}>NMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>N\cdot CH_2\cdot CO_2Me$ has been assigned.

Contrary to the statement in the previous paper (*loc. cit.*), the authors now find that piperazinediformonitrile is not reduced to piperazinedimethylenediamine, and consequently they have not, as yet, succeeded in isolating the latter compound. The only products of reduction were piperazine and ammonia. By warming a mixture of the formonitrile and aniline hydrochloride to 230—250°, *piperazinediphenylamidine*, $NPh:C(NH_2)\cdot N<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>N\cdot C(NH_2):NPh$, is obtained in glistening plates, m. p. 221—222°. It yields a crystalline *hydrochloride*, a *platinichloride*, a *mercurichloride*, $C_{18}H_{22}N_6,HgCl_2,2HCl$, and a *picrate*, m. p. 235°. Reduction of the amidine only gives piperazine, aniline, and ammonia.

W. G.

Buchner's Pyrazolinecarboxylic Acid. AUGUST DARAPSKY (*Ber.*, 1912, **45**, 797—799).—Polemical (compare Bülow, this vol., i, 134, 316; Buchner, this vol., i, 213). Bülow's azine formula is not accepted, and Buchner's original view that the condensation products of aliphatic diazo-compounds with ethylene compounds are to be formulated as pyrazolinecarboxylic acids is upheld.

E. F. A.

Reduction of Acyl Derivatives of *o*-Nitrobenzylamine. SIEGMUND GABRIEL (*Ber.*, 1912, **45**, 713—725).—The reduction of formylated derivatives of *o*-nitrobenzylamine or of *o*-nitrobenzylalkyl (aryl) amines leads to the formation of dihydroquinazolines instead of the corresponding amino-derivatives (Paal and Busch, Abstr., 1890, 71; Paal and Krecke, Abstr., 1890, 1443; 1892, 80; Gabriel and Jansen,

1890, 1442; 1892, 217). If, however, the formyl group is replaced by the acetyl or benzoyl group, the corresponding amino-derivative is formed, and may then undergo further transformation; thus, Widman (Abstr., 1893, i, 438) has shown that *o*-nitrobenzylacetanilide on reduction yields *o*-aminobenzylaniline, *o*-acetylaminobenzylaniline, and phenylmethyldihydroquinazoline. The present investigation deals with the reduction of derivatives of *o*-nitrobenzylamine, in which both the aminohydrogen atoms are replaced by a bivalent acyl group. They are found in this respect to resemble the formyl compounds.

o-Nitrobenzylsuccinimide was reduced by stannous chloride and hydrochloric acid, whereby *oxytrimethylenedihydroquinazoline*,

$$C_6H_4{<}\begin{matrix}CH_2\cdot N{-}CO\\ \quad\ \ | \\ N{=\!=}C\cdot CH_2\end{matrix}{>}CH_2$$

(m. p. 183—184°), was obtained. This can be distilled under diminished pressure, dissolves readily in acid, and is precipitated as a *hydrochloride* by excess of hydrochloric acid. It yields a crystalline *aurichloride*, *platinichloride*, and *chromate*. Its *stannichloride* and *hydriodide* were analysed.

When warmed with barium hydroxide, the base yields *barium dihydroquinazolinepropionate*, $(C_{11}H_{11}N_2O_2)_2Ba + H_2O$. From this salt *dihydroquinazolinepropionic acid* was obtained, which becomes discoloured at 205°, and has m. p. 221—223° (decomp.). When distilled in a vacuum it re-forms the base, $C_{11}H_{10}ON_2$. The *hydrochloride* of the acid softens at 200—202°, and becomes black at 240°. When an alkaline solution of the acid is oxidised with potassium ferricyanide, *quinazolinepropionic acid*, m. p. 215—217° (decomp.), after becoming discoloured at 200°, is obtained.

o-*Benzoylenedihydroquinazoline*, $C_6H_4{<}\begin{matrix}CH_2\cdot N\cdot CO\\ \quad | \quad\ \ | \\ N{=\!=}C\cdot C_6H_4\end{matrix}$, was obtained by the reduction of *o*-nitrobenzylphthalimide dissolved in glacial acetic acid with stannous chloride and hydrochloric acid. It has m. p. 182—183°, dissolves in dilute acid, and gives a precipitate of the *hydrochloride* when treated with concentrated hydrochloric acid. Its *stannichloride* was analysed. After treatment of the base with alkali (compare above), the *hydrochloride*, $C_{15}H_{12}O_2N_2,HCl$, decomposing from 220° onwards, and the *barium* salt $(+2H_2O)$ of dihydroquinazolinebenzoic acid were obtained. The free acid could not be isolated, owing to the ease with which it loses water and forms *o*-benzoylenedihydroquinazoline. On oxidation of its alkaline solution by means of potassium ferricyanide, *quinazolinebenzoic acid*, m. p. 208—209°, was obtained.

o-*Benzylenedihydroquinazoline*, $C_6H_4{<}\begin{matrix}CH_2\cdot N\cdot CH_2\\ \quad | \quad\ \ | \\ N{=\!=}C\cdot C_6H_4\end{matrix}$, was obtained by reducing *o*-nitrobenzylphthalimide dissolved in glacial acetic acid with tin and hydrochloric acid at the temperature of the boiling water-bath. Its m. p. depends somewhat on the rate of heating. It becomes red at 130°, softens at 155°, and melts at 162—164°. Its *hydrochloride* and *platinichloride* were analysed.

Reduction of dihydroquinazolinebenzoic acid in alkaline solution by means of sodium amalgam yields *tetrahydroquinazolinebenzoic acid*,

$C_6H_4<\begin{matrix}CH_2\cdot NH \\ NH-CH\cdot C_6H_4\cdot CO_2H\end{matrix}+H_2O$, which softens at 137—140°, and has m. p. 205—206°. When heated at 100°, the acid slowly loses $2H_2O$, yielding *benzoylenetetrahydroquinazoline*, $C_6H_4<\begin{matrix}CH_2\cdot N-CO \\ NH-CH\cdot C_6H_4\end{matrix}$. The same substance, m. p. 216—218°, is obtained when the tetrahydro-acid is distilled in a vacuum. Further reduction of this substance takes place when it is boiled with hydriodic acid, whereby a new *base*, $C_{15}H_{14}ON_2$, m. p. 153—154°, is obtained. Its *hydrochloride*, *hydriodide*, and *platinichloride* $(+3H_2O)$ were examined. The base is regarded as o-*aminobenzylphthalimidine*, $C_6H_4<\begin{matrix}CH_2\cdot N-CH_2 \\ NH_2\ CO\cdot C_6H_4\end{matrix}$, and this view is confirmed by its conversion, by heating with hydriodic acid or fuming hydrochloric acid at 165—170°, into benzylenedihydroquinazoline. The presence of the amino-group was established by its conversion into o-*phthaliminobenzylphthalimidine*, m. p. 204—205°. By the action of nitrous acid, the amino-group was replaced by hydroxyl with the formation of o-*hydroxybenzylphthalimidine*. For comparison the latter substance was prepared by the reduction of *salicylphthalimide* (m. p. 175—176°, obtained by heating *o*-hydroxybenzylamine with phthalic anhydride). The synthetic product softened at 155°, had m. p. 159—160°, and when mixed with the above product showed no change in m. p. H. W.

Dihydroquinazolines. XXIX. Further Study of the Stilbazoles, Hydrazones, and Schiff Bases of the 4-Dihydroquinazolone Group. MARSTON T. BOGERT and GEORGE DENTON BEAL (*J. Amer. Chem. Soc.*, 1912, **34**, 516—524. Compare Bogert, Beal, and Amend, Abstr., 1911, i, 162).—In the condensation of quinazolones with aldehydes, the alkines are either not produced under the conditions of the experiments, or are so unstable as to lose water immediately with formation of the stilbazole. The stilbazoles derived from 4-quinazolones differ from many other stilbazoles in not being easily reduced. 2-Styryl-4-dihydroquinazolone appears to be reduced to some extent by hydriodic acid and amorphous phosphorus, but a pure hydro-compound could not be isolated. Bromine reacts with the same quinazolone with formation of bromo-derivatives instead of an additive compound.

The styrylquinazolones are generally pale yellow or nearly colourless, and crystallise in fluffy masses of short, silky needles.

The following dihydroquinazolones have been prepared. 3-p-*Cyanophenyl-2-methyl-4-dihydroquinazolone*,

$$C_6H_4<\begin{matrix}N=CMe \\ CO\cdot N\cdot C_6H_4\cdot CN\end{matrix},$$

m. p. 240° (corr.), from *p*-aminobenzonitrile and acetylanthranil, forms faintly pink prisms, and when hydrolysed with potassium hydroxide is converted into the corresponding *acid*, m. p. 259° (uncorr.), which crystallises in short, yellow needles; the *ethyl* ester has m. p.

172—173° (corr.). 3-p-*Anisyl-2-methyl-4-dihydroquinazolone*,

$$C_6H_4<\begin{matrix}N{=}CMe \\ CO{-}N\cdot C_6H_4\cdot OMe\end{matrix},$$

m. p. 170° (corr.), from *p*-anisidine and acetylanthranil, forms colourless, hexagonal prisms. 3-p-*Phenetyl-2-methyl-4-dihydroquinazolone*, m. p. 148° (corr.), yields a *sulphonic acid*, not melting below 300°, the *sodium* salt of which forms a grey powder, and does not melt below 300°. 3-*Benzyl-2-methyl-4-dihydroquinazolone*,

$$C_6H_4<\begin{matrix}N{=}CMe \\ CO{-}N\cdot CH_2Ph\end{matrix},$$

m. p. 123° (corr.), from benzylamine and acetylanthranil, crystallises in colourless flakes.

By condensing the respective aldehydes with 2-methyl-4-dihydroquinazolones, which do not contain a primary amino-group, the following simple styryldihydroquinazolones have been obtained. The *hydrochloride* of 2-styryl-4-dihydroquinazolone (*loc. cit.*) has m. p. 310° (decomp.). 6-*Nitro-2-styryl-4-dihydroquinazolone*, $NO_2\cdot C_6H_3<\begin{matrix}N{=}C\cdot CH{:}CHPh \\ CO\cdot NH\end{matrix}$, m. p. 323·5° (uncorr.), obtained either by nitrating 2-styryl-4-dihydroquinazolone with fuming nitric acid, or by condensing benzaldehyde with 6-nitro-2-methyl-4-dihydroquinazolone, forms short, yellow needles. 2-o-*Nitrostyryl-4-dihydroquinazolone*,

$$C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CH\cdot C_6H_4\cdot NO_2 \\ CO\cdot NH\end{matrix},$$

has m. p. 300° (uncorr.), and 2-p-*nitrostyryl-4-dihydroquinazolone*, m. p. 350° (uncorr.). 6-*Nitro*-2-p-*nitrostyryl-4-dihydroquinazolone*,

$$NO_2\cdot C_6H_3<\begin{matrix}N{=}C\cdot CH{:}CH\cdot C_6H_4\cdot NO_2 \\ CO\cdot NH\end{matrix},$$

m. p. 335° (uncorr.), was obtained as an orange-yellow solid by the action of a mixture of fuming nitric acid and sulphuric acid on 2-styryl-4-dihydroquinazolone. *Bromo-2-styryl-4-dihydroquinazolone* decomposes at about 345°, and the *dibromo*-derivative does not melt below 300°. 2-Styryl-3-methyl-4-dihydroquinazolone (*loc. cit.*) can be prepared by the action of methyl iodide on 2-styryl-4-dihydroquinazolone in presence of potassium hydroxide. 2-*Styryl-3-ethyl-4-dihydroquinazolone*, from 2-methyl-3-ethyl-4-dihydroquinazolone and benzaldehyde, has m. p. 125° (corr.). 3-*Phenyl-2-styryl-4-dihydroquinazolone*, from 3-phenyl-2-methyl-4-dihydroquinazolone and benzaldehyde, has m. p. 201° (corr.). The following compounds were obtained in a similar manner. 3-p-*Tolyl-2-styryl-4-dihydroquinazolone*, m. p. 197° (corr.), and the corresponding 3-*benzyl* derivative, m. p. 142° (corr.), 3-p-*anisyl* derivative, m. p. 223° (corr.), 3-p-*phenetyl* derivative, m. p. 204° (corr.), 3-*α-naphthyl* derivative, m. p. 187° (uncorr.), 3-*β-naphthyl* derivative, m. p. 240° (uncorr.), and 3-*anilino*-derivative, m. p. 217° (uncorr.). 3-*Phenyl*-2-o-*hydroxystyryl-4-dihydroquinazolone*, $C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CH\cdot C_6H_4\cdot OH \\ CO\cdot NPh\end{matrix}$, m. p. 270° (uncorr.), was obtained from 3-phenyl-2-methyl-4-dihydroquinazolone

and salicylaldehyde. 2-*Methylenedioxystyryl-4-dihydroquinazolone*,

$$C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CH\cdot C_6H_3O_2{:}CH_2\\ CO\cdot NH\end{matrix},$$

m. p. 305° (uncorr.), from 2-methyl-4-dihydroquinazolone and piperonaldehyde, and 2-*phenylbutadienyl-4-dihydroquinazolone*,

$$C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CH\cdot CH{:}CHPh\\ CO\cdot NH\end{matrix},$$

m. p. 257—258° (uncorr.), from cinnamaldehyde and 2-methyl-4-dihydroquinazolone, are also described.

The following compounds were prepared by the condensation of aldehydes with amino-2-methyl-4-dihydroquinazolones. 3-*Acetylamino*-2-*styryl*-4-*dihydroquinazolone*, m. p. 259° (uncorr.), was obtained both by the action of acetic anhydride on 3-amino-2-styryl-4-dihydroquinazolone and by the condensation of 3-acetylamino-2-methyl-4-dihydroquinazolone with benzaldehyde. Attempts to effect the condensation of 3-amino-2-methyl-4-dihydroquinazolone with citral, furfuraldehyde, and glyoxal were not successful. On boiling an alcoholic solution of 3-amino-2-methyl-4-quinazolone and benzil, a *substance*, probably $C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CPh\\ CO\cdot N{-}N{:}CPh\end{matrix}$, m. p. about 292° (decomp.), separates as a yellow, granular solid. When 2-amino-4-dihydroquinazolone is heated with benzaldehyde at 180°, condensation does not take place.

An attempt to effect the condensation of 2-methyl-4-dihydroquinazolone with ethyl oxalate in presence of sodium ethoxide did not meet with success. E. G.

Dihydroquinazolines. XXX. Study of the Bromination and Nitration of 4-Dihydroquinazolones, the Corresponding Aminoquinazolones, and Certain Other New 4-Dihydroquinazolones. MARSTON T. BOGERT and GEORGE AUGUSTUS GEIGER (*J. Amer. Chem. Soc.*, 1912, **34**, 524—534).—The 4-dihydroquinazolones are not easily brominated, but bromo-derivatives of 4-dihydroquinazolone and 2-methyl-4-dihydroquinazolone have been obtained by the Juvalta process (D.R.-P. 50177). Nitration is also difficult to effect, but by using a mixture of fuming nitric acid and concentrated sulphuric acid at a high temperature, one nitro-group can be introduced into the 4-quinazolone nucleus.

3-Methyl-4-dihydroquinazolone was first prepared by Knape (Abstr., 1891, 909), who assigned to it the m. p. 71°. It has now been found that this m. p. is that of the form containing $1H_2O$, but that the anhydrous compound has m. p. 105° (corr.). 2 : 3-Dimethyl-4-dihydroquinazolone also crystallises with $1H_2O$; the m. p.'s of the anhydrous and hydrated forms are 107—109° and 70° respectively. 3-*Ethyl*-4-*dihydroquinazolone*, $C_6H_4<\begin{matrix}N{=}CH\\ CO\cdot NEt\end{matrix}$, m. p. 102° (corr.), b. p. 182°/15 mm., prepared by the action of ethyl iodide on 4-quinazolone in presence of alcohol and potassium hydroxide, crystallises in colourless needles. 2-*Benzyl*-4-*dihydroquinazolone* has m. p. 116° (corr.).

3-p-*Nitrophenyl-2-methyl-4-dihydroquinazolone*,

$$C_6H_4<\begin{matrix}N{=}CMe\\ CO\cdot N\cdot C_6H_4\cdot NO_2\end{matrix},$$

m. p. 193° (corr.), from acetylanthranil and *p*-nitroaniline, forms pale yellow, lustrous scales. 3-p-*Tolyl-2-methyl-4-dihydroquinazolone* has m. p. 151° (corr.), and the corresponding 3-*α-naphthyl* and 3-*β-naphthyl* compounds melt at 136° (corr.) and 175° (corr.) respectively.

Bromo-4-dihydroquinazolone, $C_6H_3Br<\begin{matrix}N{=}CH\\ CO\cdot NH\end{matrix}$, has m. p. 258° (uncorr.), and *bromo-2-methyl-4-dihydroquinazolone*,

$$C_6H_3Br<\begin{matrix}N{=}CMe\\ CO\cdot NH\end{matrix},$$

m. p. 277° (uncorr.).

Nitro-4-dihydroquinazolone, $NO_2\cdot C_6H_3<\begin{matrix}N{=}CH\\ CO\cdot NH\end{matrix}$, m. p. 284° (decomp.), forms silky, yellow plates; the nitro-group is probably in the 6-position. 6-*Nitro-2-methyl-4-dihydroquinazolone*,

$$NO_2\cdot C_6H_3<\begin{matrix}N{=}CMe\\ CO\cdot NH\end{matrix},$$

m. p. 299° (decomp.), obtained by the nitration of 2-methyl-4-quinazolone, crystallises in pale yellow needles. *Nitro-3-methyl-4-dihydroquinazolone*, $NO_2\cdot C_6H_3<\begin{matrix}N{=}CH\\ CO\cdot NMe\end{matrix}$, m. p. 196° (corr.), can be prepared either by the methylation of nitro-4-dihydroquinazolone or by the nitration of 3-methyl-4-dihydroquinazolone. The corresponding 3-*ethyl* compound has m. p. 165° (corr.). By the nitration of 2-methyl-3-ethyl-4-dihydroquinazolone, the 6-nitro-derivative was obtained of the same m. p. as that prepared by Bogert and Cook (Abstr., 1906, i, 988) by the action of ethylamine on 5-nitroacetylanthranil. *Dinitro-3-phenyl-2-methyl-4-dihydroquinazolone*, m. p. 267° (uncorr.), obtained by the nitration of 3-phenyl-2-methyl-4-dihydroquinazolone, is probably the 6-nitro-3-*o*-nitrophenyl compound. *Nitro*-3-p-*nitrophenyl-2-methyl-4-dihydroquinazolone* has m. p. 264° (decomp.). *Dinitro*-3-p-*tolyl-2-methyl-4-dihydroquinazolone* has m. p. 275° (decomp.).

The following amino-compounds were obtained by reducing the corresponding nitro-compounds with stannous chloride and hydrochloric acid. *Amino-4-dihydroquinazolone*, $NH_2\cdot C_6H_3<\begin{matrix}N{=}CH\\ CO\cdot NH\end{matrix}$, m. p. 318° (corr.), which yields an *acetyl* derivative, m. p. 335° (corr.). 6-Amino-2-methyl-4-dihydroquinazolone, m. p. 314—315° (corr.), identical with the compound prepared from 2 : 5-diacetylaminobenzoic acid (Bogert, Amend, and Chambers, Abstr., 1910, i, 895). *Amino-3-methyl-4-dihydroquinazolone*, $NH_2\cdot C_6H_3<\begin{matrix}N{=}CH\\ CO\cdot NMe\end{matrix}$, m. p. 209° (uncorr.), which yields an *acetyl* derivative, m. p. 269° (uncorr.). 6-*Amino-2 : 3-dimethyl-4-dihydroquinazolone*, m. p. 244° (uncorr.). 6-*Amino-2-methyl-3-ethyl-4-dihydroquinazolone*, m. p. 185° (corr.).

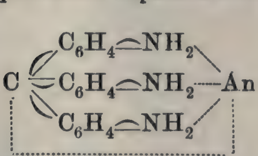
2-Methyl-4-dihydroquinazolone is not appreciably affected when heated for six hours with concentrated hydrochloric acid at 155°,

slight decomposition occurs at 190°, and at 250° it is completely decomposed into aniline, ammonia, and carbon dioxide. An attempt to prepare 4-chloro-2-methylquinazoline by the action of benzoyl chloride on 2-methyl-4-dihydroquinazolone (2-methyl-4-hydroxyquinazoline) was not successful. E. G.

Indigotindisulphonic Acid, Atmospheric Oxygen and Hydroxyl Ions. M. TSCHILIKIN and W. MILANOWSKY (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 359—373).—According to Friedländer's investigations on the action of alkali on indigotin, the principal products of the reaction are indoxyl-2-aldehyde and anthranilic acid, the chrysanilic acid formed being the result of a secondary condensation of these two products; these results were confirmed by similar experiments on "thioindigo" (*Ber.*, 1877, **10**, 1971).

The authors have investigated the action of alkali hydroxide on indigotindisulphonic acid, in which the blue colour of the latter is destroyed. They find that the action of the alkali is mainly a catalytic effect of the hydroxyl ions, and that the reaction depends also on the presence of atmospheric oxygen and is of an order varying with the number of molecules of oxygen available. When the concentration of atmospheric oxygen dissolved in the solution is kept constant, the reaction is unimolecular. These results are not in agreement with the scheme of the reaction given by Friedländer. T. H. P.

Constitution of Triphenylmethane Dyes. HUGO KAUFFMANN (*Ber.*, 1912, **45**, 781—786).—The author points out objections to the quinonoid representation of the constitution of the triphenylmethane-dyes, and emphasises the advantages of his formulæ, which are based on the auxochromic theory and the theory of the divisibility of the valency bond. Pararosaniline, for example, is represented by the annexed formula, in which An denotes a univalent anion and the dotted lines denote the divisions of the valency bond of the univalent anion. The total affinity represented by the dotted lines corresponds with one valency unit. C. S.



Precipitate Produced by Mercuric Acetate from Molasses. Isolation of Adenine. STOLTZENBERG (*Zeitsch. Ver. deut. Zuckerind*, 1912, 318—322).—After clarifying molasses with lead acetate the precipitate produced by mercuric acetate does not contain any substance of high optical rotatory power in neutral solution. Lævorotatory substances could not be detected; some constituents of the precipitate were dextrorotatory in solution in hydrochloric acid. The precipitate contains at least two acids and two bases, but aspartic acid is not present. The chief product is adenine. E. F. A.

The Action of Arsenites and Cyanide-Sulphides on Diazo-compounds. AUGUST GUTMANN (*Ber.*, 1912, **45**, 821—832. Compare Abstr., 1898, ii, 570; 1907, i, 671; 1908, i, 497, 597, 972; 1909, i, 128, 144, 895).—From his earlier results on the addition of oxygen

or sulphur to an alkali arsenite or to a mixture of alkali cyanide and sulphide, from thiosulphates, thiosulphonates, alkyl nitrates, etc., the author is of opinion that the reactive oxygen, sulphur, or chlorine atom is present in a special form of a higher valency than the usual. Similar active atoms are found in some of the diazo-compounds.

Sodium arsenite solution is oxidised to arsenate by both benzenediazonium chloride solution and sodium benzene-*n*-diazo-oxide solution, whilst the latter also oxidises a mixture of potassium cyanide and sodium sulphide to thiocyanate; benzene and nitrogen are also formed in each reaction, but in the last reaction a thiodiazo-compound,

$$Ph\cdot N_2\cdot SNa,$$

is probably an intermediate product (compare Hantzsch and Freese, Abstr., 1905, i, 24). Solutions of *p*-nitrobenzenediazonium chloride and of potassium *p*-nitrobenzene-*n*-diazo-oxide likewise reacted with sodium arsenite, but the reaction was far from quantitative. Potassium benzene *iso*diazo-oxide, potassium *p*-nitrobenzene *iso*diazo-oxide, azoxybenzene, *p*-hydroxyazobenzene, diazoaminobenzene, azobenzene, nitrosodimethylaniline, nitrosophenol, and phenylnitrosoamine were stable towards sodium arsenite.

A suspension of the labile potassium benzenediazosulphonate (Bamberger, Abstr., 1905, i, 25) reacted with sodium arsenite and with the cyanide-sulphide mixture, whereas the stable isomeride did not react either in acid or alkaline solution. Sodium benzene-*n*-diazo-oxide was unaffected by sodium sulphite solution, but benzenediazonium chloride solution treated with barium chloride and sulphur dioxide caused precipitation of barium sulphate. It is suggested that the labile diazosulphonate may be formulated $Ph\cdot N_2\cdot \ddot{O}\cdot SO_2K$, whilst the stable isomeride may be of the ordinary sulphonate structure

$$Ph\cdot N_2\cdot SO_2\cdot OK.$$

The di-potassium derivative of *p*-sulphobenzenediazohydroxide,

$$SO_3K\cdot C_6H_4\cdot N_2\cdot OK,$$

oxidises arsenite to arsenate and the cyanide-sulphide reagent to thiocyanate. The final products of reaction are nitrogen and a salt of benzenesulphonic acid, but in the reaction with cyanide-sulphides, a salt of *p*-sulphobenzenediazonium hydrosulphide, $SO_3H\cdot C_6H_4\cdot N_2\cdot SH$, is probably an intermediate step (compare Klason, Abstr., 1887, 478).

Diazobenzene perbromide and diazobenzeneimide oxidise both the above reagents, the main organic products being bromobenzene and aniline respectively. Hydrazoic acid does not show similar oxidising power.

Nitrosoacetanilide and benzoylphenylnitrosoamine both act as oxidising agents towards the two reagents used, and it is therefore suggested that their structure is similar to that of the labile diazo-oxides and should be written $R\cdot N\!:\!N\cdot OAc$. D. F. T.

endo-**Azo-compounds.** Henri Duval (*Compt. rend.*, 1912, 154, 780—781. Compare Abstr., 1907, i, 663; 1908, i, 706).—The only *oo*-diamino-derivatives of diphenylmethane hitherto known to form *endo*-azo-compounds are those with a carbon-containing group in the para-position. It is now found that other electronegative radicles

confer the power of forming these substances, and that the presence of one amino-group is sufficient to admit of their formation.

4 : 4-*Dichloro*-2 : 2-*bis*endo*azodiphenylmethane*,

$$\begin{array}{c}C_6H_3Cl\\ |\\ N{=\!=\!=}N\end{array}\!\!>C<\!\!\begin{array}{c}C_6H_3Cl\\ |\\ N{:}N\end{array},$$

prepared by diazotising dichlorodiaminodiphenylmethane and heating to 80°, separates from pyridine in orange crystals, decomposing at about 300°.

When *o*-acetylaminodiphenylmethane is treated at 5° with sulphuric and fuming nitric acids, two nitro-derivatives are formed and may be separated by alcohol. *Dinitro*-o-*acetylaminodiphenylmethane* has m. p. 265°, whilst the *trinitro*-derivative has m. p. 213°. Hydrolysis followed by diazotisation converts these substances into *dinitro*-o-endo*azodiphenylmethane*, $\begin{array}{c}(NO_2)_2C_{12}H_7\\ |\\ N{:}N-\end{array}\!\!>CH$, m. p. 324°, and *trinitro*-o-endo*azodiphenylmethane*, m. p. 248°. W. O. W.

Azo-dyes of Substituted Pyrroles. LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1912, **77**, 247—248).—A reply to Fischer and Bartholomäus (this vol., i, 323). It was shown (Abstr., 1908, i, 710) beyond question that the azo-dye from hæmopyrrole was a diazo-compound. Hæmopyrrole also forms a monoazo-dye with benzene-diazonium chloride crystallising in orange-yellow needles, which in presence of excess of the diazonium salt pass over into the reddish-brown needles of the diazo-compound. E. F. A.

Investigations by means of the Dilatometer on the Heat Coagulation and Solution of Albumin. TULLIO GAYDA (*Biochem Zeitsch.*, 1912, **39**, 400—409).—The thermal expansion of pure albumin is greater than that of water. The volume changes taking place when the temperature is very slowly raised during coagulation are very small. Below the coagulation temperature, the rate of increase of volume change is greater below the clotting temperature, and remains so whilst the clot is forming, giving rise to a slower rate of increase as the albumin reaches the stage of complete coagulation. During the solution of albumin a contraction of volume takes place. This is possibly due to a true solution of the water in the substance of the colloidal particles. S. B. S.

Proteins of Liebig's Extract of Meat. KARL MAYS (*Zeitsch. physiol. Chem.*, 1912, **78**, 37—52).—Liebig's extract of meat contains a non-coagulable protein, which closely resembles glutin in its reactions, and has many reactions in common with the albumoses. It yields glycine and proline, but not glutamic acid on hydrolysis. The protein is formed during the cooking of the meat with water at 80—94° in the commercial preparation of the extract. E. F. A.

The Action of Various Conditions on Carboxyhæmoglobin. H. HARTRIDGE (*J. Physiol.*, 1912, **44**, 22—33).—Dilution, carbon dioxide, and certain salts have no influence on

the final saturation of hæmoglobin with carbon monoxide. Light, especially ultra-violet rays, lessens the stability of carboxyhæmoglobin, and temperature has a marked influence, the change in saturation being about 0·5% for every degree rise. Equilibrium is reached at different saturations by the blood of animals of different species. W. D. H.

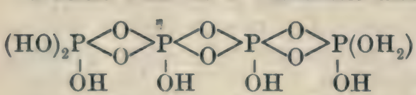
Heat Coagulation of Hæmoglobin Compounds. H. HARTRIDGE (*J. Physiol.*, 1912, **44**, 34—42).—The results obtained with oxyhæmoglobin confirm those of Chick and Martin, and apply also to carboxyhæmoglobin. The temperature-coefficient of the latter is 1·18, and so it is comparatively stable. Nitric oxide-hæmoglobin is unstable, and tends to change spontaneously at room temperature into alkaline methæmoglobin; alkaline methæmoglobin has a temperature-coefficient higher than that of oxy- or carboxy-hæmoglobin, being near to that of egg-albumin. W. D. H.

Formation of Nucleic Acids from the Thymus Gland. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1912, **77**, 497—507).—Sodium nucleate when dried over sulphuric acid and heated, continues to lose water until it decomposes. Preparations of constant composition containing water of crystallisation, dried by means of absolute alcohol and ether, have been analysed. Those prepared by different workers agree closely, and correspond with the formula

$$C_{43}H_{53}O_{30}N_{15}P_4Na_4,11H_2O$$

put forward in 1907 (Steudel, Abstr., 1907, i, 168, 1097), or still better with the formula $C_{43}H_{53}O_{32}N_{15}P_4Na_4,11H_2O$, deduced from the products of the quantitative hydrolysis of nucleic acid.

Nucleic acid as a tetrabasic acid is derived from the annexed phosphoric acid skeleton, and the correct formula becomes $C_{43}H_{61}O_{34}N_{15}P_4,9H_2O$. During drying more water than $9H_2O$ will probably tend to be eliminated.



Thymus-nucleic acid behaves differently from yeast-nucleic acid as regards the formation of vernine (guanosine) on hydrolysis. From thymus-nucleic acid a quantity of guanine corresponding with the inorganic phosphorus liberated is produced. Apparently the hexose is much less firmly united to the alloxuric bases than is the pentose with the purine compounds in yeast-nucleic acid. E. F. A.

Tannage by means of Halogens. L. MEUNIER and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1912, [iv], **11**, 344—347).—Lumière and Seyewetz have shown already (Abstr., 1908, i, 710) that gelatin is rendered "insoluble" (tanned) by halogens, and in the present paper the best conditions for accomplishing this are described (compare Cross, Bevan, and Briggs, Abstr., 1908, i, 374).

Gelatin cannot be rendered insoluble with gaseous chlorine, as it undergoes decomposition under these conditions, and the same is true of chlorine water at atmospheric temperatures. Good results are

obtained by macerating gelatin (10 grams) at 0° in (1) 500 c.c. of chlorine water, containing 50 grams of sodium chloride, or (2) 100 c.c. of commercial sodium hypochlorite solution, diluted with 400 c.c. of water, and containing 2 c.c. of hydrochloric acid (21°B). Under these conditions the gelatin absorbs 9% of chlorine; this can be reduced to 0·3% by washing with 10% sodium hydrogen sulphite solution, and the gelatin remains insoluble after this treatment. Similar results are obtained by using (*a*) 100 c.c. of bromine water, diluted to 500 c.c. with water and containing 100 grams of sodium chloride, or (*b*) bromine 3 grams, sodium hydroxide 1·5 grams in 500 c.c. of water. Iodine and hypoiodites have no action of this kind on gelatin. Skin may be rapidly tanned by the use of bromine water in presence of sodium chloride, the bromine being subsequently removed by washing with sodium hydrogen sulphite. The action probably consists in the formation of halogenated amino-groups in the protein molecule. T. A. H.

Condensation of Tryptophan with Certa i Aldehydes. ANNIE HOMER (*Proc. Camb. Phil. Soc.*, 1912, **16**, 405—408).—When tryptophan is kept in contact with moist ether which has been locally heated with a glass rod, a crystalline compound, $C_{24}H_{26}O_5N_4$, of acidic nature, m. p. 322°, is obtained.

The compound, $C_{12}H_{12}O_2N_2$, from formaldehyde and tryptophan has m. p. 235—240°; it is readily hydrolysed by water, dilute acids, and alkalis to form the ether oxidation product above.

Glyoxylic acid reacts with tryptophan to form a crystalline derivative, $C_{13}H_{11}O_4N_2$, m. p. 322°. When heated at 205°, carbon dioxide is evolved, and the ether oxidation product is obtained.

Formaldehyde is shown to play an important part in the colour reaction of tryptophan with concentrated sulphuric acid, and this rather than glyoxylic acid is the substance essential to the formation of the characteristic violet colour in the Adamkiewicz reaction.

E. F. A.

Plasteins. J. HERRMANN and A. CHAIN (*Zeitsch. physiol. Chem.*, 1912, **77**, 289).—Plasteins injected into rabbits yield an antiserum which precipitates them. As only proteins act as antigens in the precipitin reaction, this is regarded as a proof of the protein nature of the plasteins. Various plasteins give precipitates with the same antiserum; this is a proof of a similarity in their structure.

W. D. H.

Nitrosalmine. E. WECHSLER (*Zeitsch. physiol. Chem.*, 1912, **78**, 53—54. Compare Kossel and Kennaway, Abstr., 1911, i, 667; Kossel and Cameron, this vol., i, 326).—Salmine forms a nitro-derivative which on hydrolysis with boiling sulphuric acid is converted into nitroarginine. E. F. A.

Activity of the Sucrase of "Aspergillus" in Presence of Different Acids. GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Compt. rend.*, 1912, **154**, 837—839).—A tabular statement gives the concentration of different organic and inorganic acids, in the presence of which the sucrase of *Aspergillus niger* shows its maximum

diastatic activity. The conclusions drawn are precisely similar to those set forth in recent communications on the sucrase of yeast (this vol., i, 148, 327). The optimum concentrations of acids for the enzyme from the two sources are very different. W. O. W.

Diastase. T. CHRZASZCZ (*Woch. Brauerei*, 1911, 28, 510).—A preliminary note on work which the author has in progress on barley extracts, from which he assumes that diastase consists of two distinct substances that are differently acted on by starch. F. M. G. M.

The Influence of Lecithin and Lipoids on Diastase. D. MINAMI (*Biochem. Zeitsch.*, 1912, 39, 355—380).—Lecithin even in very small concentrations in aqueous suspension inhibits the action of diastase. In methyl-alcoholic solution lecithin inhibits the pancreatic and salivary diastase. In the case of serum diastase, the methyl-alcoholic solution was in one case without influence, and in another case it exerted an activating action. The amounts of methyl alcohol alone used in these experiments were without action. The serum alone has, however, an activating tendency, and it was found that a lecithin-serum mixture was less active than the serum alone. The phosphatides of the liver activate diastases; the substances exerting this action are soluble in ether, benzene, and light petroleum. Weak aqueous alcoholic suspensions of the acetone extract of liver inhibited diastatic action. The expressed juice of liver exerts an activating influence, which does not appear to be due to the phosphatides. The activating influence of serum on diastase is very slightly diminished by extracting it with ether. This is, however, due to the ether alone, which remains dissolved in the serum. The phosphatides of egg-yolk act as an activator. This activator is soluble in ether. The author is unable to agree with the statement of Bang that diastatic action depends on the action of lipoids. S. B. S.

The Influence of Bile on Diastase (Amylase). D. MINAMI (*Biochem. Zeitsch.*, 1912, 39, 339—354).—The bile by itself has only a small diastatic power, but it can activate amylase. The activator is soluble in water and alcohol, but not in ether; the ethereal extract, on the other hand, exerts an inhibiting influence, both alone and in presence of alcoholic and aqueous extracts. Sodium taurocholate and cholate are without action on diastase in weak solutions and inhibit the action in strong solutions. Sodium glycocholate in two instances exerted a slight activating action on salivary diastase, but acted like the other bile salts on pancreatic diastase. Cholesterol exerted an inhibitory action, especially in presence of lecithin. The action of the bile pigments was also inhibitory. S. B. S.

Takadiastase. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1912, 39, 324—338).—The amylase of taka-diastase is not so sensitive to the action of acids as the amylase of saliva, in that it requires stronger concentrations of acid to produce a corresponding inhibition of its action. It is sensitive to alkalis also, but again this sensitiveness is less than in the case of the salivary amylase. The amylase action of taka-diastase

is accelerated by the presence of many salts in the concentration of $N/10$, smaller concentrations having little or no influence. Taka-diastase exerts a tryptic action which is stronger in weak alkaline or neutral solutions than in slightly acid solutions. Sera inhibit the action. It contains a milk-clotting enzyme of chymosin-like character. It contains no peptolytic ferment (action on glycyltryptophan), whereas it has a strong ereptic power. This fact is regarded as a proof that the so-called peptolytic and ereptic ferments are not identical. Taka-diastase also contains a lipase, which can hydrolyse neutral fats, monobutyrin, and lecithin, but it is not present in large quantities. It also contains an adrenalase. One gram of the diastase contains as much trypsin as 100 c.c. of human pancreatic juice. S. B. S.

Quantitative Measurement of Oxydases. HERBERT H. BUNZEL (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxvi; *J. Biol. Chem.*, 11).—Measurements were made of the oxidising power of potato juice towards a series of aromatic substances. If two or three oxidisable substances were used in the same experiment, the result is not a summation of the individual oxidations when the oxidation by the same juice is measured separately, but corresponds roughly with the result obtained in the case of the most rapidly oxidised substance.

W. D. H.

The Separation of Peroxydase and Catalase. A. KASANSKI (*Biochem. Zeitsch.*, 1912, **39**, 64—71).—Advantage is taken of the fact that the catalase becomes inactive when treated with pyrogallol. If, for example, the juice from hemp seedlings is treated with pyrogallol in sufficient quantity (2%), a precipitate is formed. Neither the precipitate nor the filtrate contain a catalase, although a peroxydase is present in the latter. Examples are given of the application of the pyrogallol method for the preparation of catalase-free peroxydase from various sources. S. B. S.

The Mode of Action of Phosphatese. II. HANS VON EULER and HJ. OHLSÉN (*Zeitsch. physiol. Chem.* 1912, **76**, 468—477. Compare Abstr., 1911, i, 1051).—When a 20% solution of dextrose, dried yeast extract, and 5% disodium phosphate solution are mixed, no disappearance of the inorganic phosphate takes place as a rule. When, however, the dextrose solution is set to ferment for a few minutes with living yeast, then filtered and boiled before the addition of the dried yeast extract and phosphate, there is a rapid and complete disappearance of inorganic phosphate, which is converted into hexosephosphate. Yeast dried by Lebedeff's process slowly effects the same change without previous fermentation of the dextrose. Thymol acts adversely on the change, but toluene is without effect.

If the preliminary fermentation of the dextrose is prolonged, the rate of esterification becomes very much less. An excess of disodium phosphate also retards esterification. The addition of the sodium salt of the hexosephosphate very markedly accelerates the rate of ester-formation. It has a similar accelerating effect on the fermentation of dextrose by living yeast, being about ten times as effective as an addition of a like quantity of disodium phosphate. E. F. A.

Dibenzyl- and Diphenyl-silicols and -silicones. GEOFFREY MARTIN (*Ber.*, 1912, **45**, 403—409. Compare Dilthey and Eduardoff, Abstr., 1904, i, 464; Robison and Kipping, Trans., 1908, **93**, 439).—The more easily fusible isomeric form of dibenzylsilicol,

$$Si(CH_2Ph)_2(OH)_2$$

(m. p. 74°), is convertible into the other (m. p. 101°) by the action of aqueous potassium hydroxide on the solution in methyl or ethyl alcohol, and subsequent precipitation by acetic acid.

If dibenzylsilicol (m. p. 101°) is treated with water in a closed vessel at 100°, or a solution in aqueous potassium hydroxide exposed to the air, a white, amorphous dibenzylsilicone, $SiO(CH_2Ph)_2$, is obtained. A different form of this substance is obtained by exposing to the air the gummy mass obtained by the action of dilute ammonia on dibenzylsilicon chloride; the product is a white mass, m. p. approx. 200°.

Diphenylsilicol, $SiPh_2(OH)_2$, obtained by the action of dilute ammonia solution on diphenylsilicon chloride, is a white, crystalline substance, m. p. varying in different specimens from 140° to 160°; a specimen of m. p. 160° dissolved in dilute potassium hydroxide solution and reprecipitated by acid gave a product m. p. approx. 144°, probably identical with that obtained by Dilthey (*loc. cit.*); when this is dissolved in a little methyl alcohol and warmed with a large excess of potassium hydroxide, the precipitate obtained on acidifying consists of the original form (m. p. 160°). Both these forms of diphenylsilicol when heated alone, or when left in contact with dilute hydrochloric acid, give a pasty, amorphous silicone; when heated with acetic anhydride, this is converted into a crystalline silicone, m. p. 188°, probably identical with that obtained by Dilthey. By dissolving either form of diphenylsilicol in glacial acetic acid and afterwards reprecipitating by water, an amorphous substance is produced, which, after purification, has m. p. 111°.

The author confirms Dilthey's statement as to the existence of two forms of termolecular diphenylsilicone, and in addition has obtained small quantities of two other crystalline substances, m. p. 125° and 186° respectively. Another form of diphenylsilicone (m. p. above 360°) was obtained: (*a*) by the prolonged action of methyl-alcoholic potash on diphenylsilicol, previously heated to 140°; (*b*) by warming diphenylsilicol with potassium hydroxide solution for several hours at 100°.

Phenylbenzylsilicon chloride, $SiPh(CH_2Ph)Cl_2$, obtained by the action of magnesium phenyl bromide on benzylsilicon trichloride, is a colourless liquid, b. p. 240—250°/100 mm.; on treatment with dilute ammonia solution it gives a white solid, which, when placed in contact with potassium hydroxide solution, dissolves partly; the solution on acidifying precipitates *phenylbenzylsilicol*, m. p. 104°, after repeated recrystallisation. D. F. T.

Organic Chemistry.

γ-Ethylhexane. LATHAM CLARKE and EMILE RAYMOND RIEGEL (*J. Amer. Chem. Soc.*, 1912, **34**, 674—679).—In continuation of a study of the paraffin hydrocarbons (this vol., i, 150, and earlier abstracts), the synthesis of γ-ethylhexane has been effected.

γ-Ethylhexan-γ-ol, $CH_2Me\cdot CEt(OH)\cdot CH_2\cdot CH_2Me$, b. p. 155—159°/756 mm., prepared by the action of magnesium propyl iodide on diethyl ketone, has an odour resembling that of musty apples. On treating this compound with iodine and amorphous phosphorus, *γ-iodo-γ-ethylhexane*, $CH_2Me\cdot CEtI\cdot CH_2\cdot CH_2Me$, is produced, which is converted by alcoholic potassium hydroxide into *γ-ethyl-Δ^{β}-hexene*, $CHMe\colon CEt\cdot CH_2\cdot CH_2Me$, b. p. 119·6—120·5°/769 mm., a liquid with a strong odour. When the latter compound is passed over freshly reduced nickel at 160—180° in a current of hydrogen, *γ-ethylhexane*, $CH_2Me\cdot CHEt\cdot CH_2\cdot CH_2Me$, b. p. 118·8—119°/766 mm., D_{15}^{15} 0·7175, n_D^{25} 1·3993, is obtained as a colourless, very mobile, almost odourless liquid.

A second method was devised for the synthesis of the hydrocarbon which involved the preparation of ethyl ethylpropylacetoacetate and its hydrolysis with formation of γ-ethylhexan-β-one, the reduction of the latter into γ-ethylhexan-β-ol, and the conversion of this into the corresponding carbinyl iodide. The iodide on treatment with alcoholic potassium hydroxide should yield γ-ethyl-β-hexene, which would then be reduced to γ-ethylhexane. The method was not carried out completely, however, owing to the difficulty of obtaining a sufficient quantity of γ-ethylhexan-β-one.

γ-Ethylhexan-β-one, $CH_3\cdot CO\cdot CHEt\cdot CH_2\cdot CH_2Me$, b. p. 157·5—158·5°/761 mm., is a liquid with a peppermint-like odour, and on reduction is converted into *γ-ethylhexan-β-ol*, $CH_3\cdot CH(OH)\cdot CHEt\cdot CH_2\cdot CH_2Me$, b. p. 167·5—168·5°/760 mm., which has an odour resembling that of musty apples.

E. G.

δ-Methyloctane. LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1912, **34**, 680—683).—In earlier papers (this vol., i, 150), the synthesis of two nonanes, namely, $\beta\delta$- and $\beta\epsilon$-dimethylheptanes, has been described. An account is now given of the synthesis of δ-methyloctane.

When methyl butyl ketone is treated with magnesium propyl iodide, δ-methyloctan-δ-ol and δ-methyleneoctane are produced in proportions depending on the conditions of the experiment. A method is described by which the methyleneoctane can be obtained in a yield of about 80% of the theoretical. *δ-Methyloctan-δ-ol*,

$$CH_2Me\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CH_2Me,$$

b. p. 178—183°, is a colourless, oily liquid, with a sweet aromatic odour. *δ-Methyleneoctane*, $CH_2Me\cdot CH_2\cdot C(\colon CH_2)\cdot CH_2\cdot CH_2\cdot CH_2Me$, b. p. 142—144°/768 mm., is a liquid with a faint, sweet odour; when passed over freshly reduced nickel at 160—180° in a current of hydrogen, it is converted into *δ-methyloctane*,

$$CH_2Me\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2Me,$$

b. p. 141·7—141·9°/771 mm., D_{15}^{15} 0·7320, n_D^{25} 1·4027, which is a colourless, almost odourless, very mobile liquid. E. G.

Preparation of Isoprene. CARL HARRIES (D.R.-P. 243075 and 243076).—Isoprene having a refractive index of 52°15′—52°50′ and suitable for the preparation of caoutchouc is produced when the dihalogen or halogen-hydrin derivatives of *iso*pentane are slowly dropped on to soda-lime (or other basic oxides) at a temperature of about 600°. The following substances may be employed for this reaction: amylene dichloride, $CMe_2Cl·CHMeCl$, or the corresponding dibromide; amylene chlorohydrin, $OH·CMe_2·CHMeCl$; the bromohydrin or other allied crude substances obtainable from amylene, $CMe_2:CHMe$, by halogenation. The yield of isoprene from the bromides is 50—60%, that from the chlorides 30—40% of the theory.

The second patent states that $\alpha\delta$-dibromo-β-methylbutane,

$$CH_2Br·CHMe·CH_2·CH_2Br,$$

and dichloro*iso*pentane, $CH_2Cl·CMeCl·CH_2Me$, can also be employed in the above reaction, that their vapour can be drawn over the strongly heated oxide, and that this may be replaced by a carbonate or other halogen eliminating agent. F. M. G. M.

The Function of the Sulphhydryl Group in the Decomposition of Iodoform in the Animal Organism. TORSTEN THUNBERG (*Skand. Arch. Physiol.*, 1911, 25, 343—346).—When cysteine hydrochloride or thiolactic acid is heated at 37° with a suspension of iodoform in gum arabic solution, iodine is liberated and may be detected after a few hours. The action is attributed to the sulphhydryl (SH) group, and attention is drawn to the probability that this group takes part in the decomposition of iodoform in the animal body.

A new reaction for cysteine is given, namely, a red coloration with nitrous acid. This reaction is not specific for cysteine, but is also given by thiolactic acid and by other thio-compounds. W. J. Y.

Catalytic Dehydration of Alcohols. JEAN B. SENDERENS (*Ann. Chim. Phys.*, 1912, [viii], 25, 449—529).—In this paper the author considers in detail the dehydration of alcohols by metals and non-metals, oxides, and salts and the products formed in these reactions, and discusses the influence of temperature and the mode of action of the catalytic agents. The data utilised have been given in great part already in the following papers: Abstr., 1907, i, 577; 1907, ii, 248; 1908, i, 494, 495; 1908, ii, 166; 1909, i, 127, 286, and 1910, i, 649, but a number of new observations are also recorded, as well as results obtained by other chemists.

In their activity towards ethyl alcohol, the catalytic agents are divided into two groups, "good" and "medium." The former decompose ethyl alcohol at 250—270°, and at 340° furnish from 60 to 90 c.c. of ethylene per minute. Examples of these are aluminium silicate, "modelling clay," anhydrous aluminium sulphate, and alumina. The second group begins to decompose alcohol at 320°, and at 340° yields from 2 to 9 c.c. of ethylene per minute. Examples of these are

dicalcium and tricalcium phosphates, dimagnesium and aluminium phosphates. Intermediate between the two groups are precipitated silica and magnesium pyrophosphate. T. A. H.

Preparation of Alkyl Esters of Metaphosphoric Acid. KURT LANGHELD (D.R.-P. 242613).—*Ethyl metaphosphate*, $PO_2 \cdot OEt$, can be readily prepared by boiling together equal parts of phosphoric oxide and ether (which has been dried over sodium) during three days; a clear syrup is formed which is separated, dissolved in chloroform, and precipitated therefrom with ether; this ester is readily hydrolysed by cold alkali hydroxides, and is of therapeutic value.

F. M. G. M.

The Constituents of Ozone. CARL D. HARRIES (*Ber.*, 1912, **45**, 936—944).—The presence of oxozone (O_4) in ordinary ozone (compare this vol., ii, 343) is confirmed by a comparison of the effect produced on ethylenic substances by ordinary ozone and ozone previously washed with concentrated sulphuric acid and sodium hydroxide solution. It also provides an explanation of the frequently discordant descriptions of the ozonides obtained by various investigators.

The ozone used was, when first formed, of 11—14% strength, but treatment with sulphuric acid and sodium hydroxide reduced this, so that the "washed" ozone varied from 4·8 to 9·3%.

s-Butylene with "washed" ozone gave the normal *ozonide*,

$$\begin{array}{c}CHMe\cdot CHMe\\ \diagdown_{O_3}\diagup\end{array},$$

a mobile oil distillable in a vacuum, together with a syrupy *dimeric* product, $(C_4H_8O_3)_2$, which was not distillable. "Unwashed" ozone gave a mixture of the above ozonide with a liquid *oxozonide*,

$$\begin{array}{c}CHMe\cdot CHMe\\ \diagdown_{O_4}\diagup\end{array},$$

and a viscous *dimeric* oxozonide, $(C_4H_8O_4)_2$.

[With RICHARD SEITZ.]—"Washed" ozone forms with ethylenic substances normal ozonides instead of oxozonides or mixtures of the latter with ozonides; for example, *cyclo*hexene in hexane solution (compare Harries and Neresheimer, Abstr., 1906, i, 833) gives a white *ozonide* (m. p. 60—65°), which is probably $(C_6H_{10}O_3)_2$, together with the normal monomeric *cyclo*hexene ozonide, which is a pungent oil (b. p. 59—60°/12 mm.).

Pinene (compare Harries and Neresheimer, Abstr., 1908, i, 194) similarly gives a solid *ozonide*, probably $(C_{10}H_{16}O_3)_2$, together with an oily ozonide, probably the monomeric $C_{10}H_{16}O_3$.

Terpineol gives only a white solid *ozonide*, $C_{10}H_{17}(OH)O_3$.

Citronellol (compare Harries and Himmelmann, Abstr., 1908, i, 662) gives a viscous ozonide, $C_{10}H_{19}(OH)\cdot O_3$; the ozonides previously obtained from terpineol and citronellol ($C_{10}H_{16}O_6$ and $C_{10}H_{20}O_6$? respectively) must have been formed with an accompanying loss of a molecule of water.

Cholesterol (compare Dorée and Gardner, Trans., 1908, **93**, 1328; Diels, Abstr., 1908, i, 728; Molinari and Fenaroli, Abstr., 1908, i,

882) whether in carbon tetrachloride or hexane solution gave a microcrystalline ozonide, $C_{27}H_{45}(OH)\cdot O_8$.

[With FRITZ HAGEDOR.]—When caoutchouc is treated with "washed" ozone, the product is the earlier described syrupy unimolecular diozonide, $C_{10}H_{16}O_6$; but with the unwashed 14% ozone, the chief product, although somewhat resembling the last, is less viscous and more easily soluble, and its analysis indicates the formula $C_{10}H_{16}O_8$, namely, a *dioxozonide*. The dioxozonide on treatment with water yields more lævulic acid than aldehyde, the reverse being the case with the diozonide (compare Abstr., 1904, i, 757; 1905, i, 364).

D. F. T.

Preparation of Formic Acid from Alkali Formates. CHEMISCHE FABRIK GRÜNAU LANDSHOFF & MAYER, EMIL FRANKE AND WALTER KIRCHNER (D.R.-P. 243225).—When the Solvay process is applied to commercial sodium formate, the following reaction takes place: $HCO_2Na + H_2O + NH_3 + CO_2 = NaHCO_3 + HCO_2\cdot NH_4$.

The ammonium formate is readily separated from traces of hydrogen sodium carbonate by evaporation or sublimation, and on decomposition furnishes formic acid in a pure condition. F. M. G. M.

Preparation of Solutions of Aluminium and Chromium Formates. ALBERT WOLFF (D.R-P. 244320).—When dry sodium formate is added to moderately concentrated solutions of chromium (about 30% Cr_2O_3) or aluminium sulphates, double decomposition occurs, and the sodium sulphate is quantitatively precipitated from the solution, which can be concentrated in a vacuum at temperatures not exceeding 40°, and to a density of 41° Bé in the case of chromium or to 32° Bé when aluminium is employed. F. M. G. M.

Action of Acetic Anhydride on Nitrates. ERNST SPÄTH (*Monatsh*, 1912, **33**, 235—251).—Metallic nitrates with water of crystallisation interact readily, either in the cold or on warming, with acetic anhydride, forming the corresponding anhydrous acetates (compare Vanino, Abstr., 1911, ii, 898). The reaction is accelerated catalytically by acids, and also apparently by water, as the same nitrates in the anhydrous state do not react so readily. Nitrates which do not form hydrates at the ordinary temperature do not react in the same way with acetic anhydride; the reaction appears to depend on the unsaturated character of the hydrated nitrates.

Anhydrous magnesium, cadmium, ferric, cobalt, manganic, cupric, and chromic acetates have been prepared for the first time.

Cupric acetate is blue, cuprous acetate colourless. *Cadmium acetate* forms colourless, slender plates, m. p. 254—256°. Anhydrous *magnesium acetate* is a colourless salt, m. p. 323°. *Cerium acetate* has m. p. 308°. *Manganic acetate* forms a brown, crystalline crust. *Ferric acetate* crystallises in lustrous plates of a sealing-wax red colour, and decomposes when heated. *Cobalt acetate* forms red crystals which sublime at 260—300°/15 mm. in a current of hydrogen. Nickel acetate has a whitish-green colour. *Chromic acetate* forms a green, crystalline powder.

Only small proportions of acetate were obtained by this method in the case of sodium, potassium, strontium, barium, thallium, lead, and silver nitrates. E. F. A.

Hydrolysis of Fats by Sulphuric Acid. ADOLF GRÜN and OCTAVIAN CORELLI (*Zeitsch. angew. Chem.*, 1912, 25, 665—670, 947).—Apart from Reimer and Will's observation that old Turkey-red oil contains dierucin, it has not been observed previously that the hydrolysis of the triglycerides takes place through the $\alpha\beta$-diglycerides. The authors find that both tripalmitin and tristearin are hydrolysed by sulphuric acid with the production of the corresponding diglycerides and the free acids; probably the sulphuric acid ester of the diglyceride is first formed in each case, but this could not be isolated.

$\alpha\beta$-Distearin sulphate was obtained as a soft, microcrystalline mass by treating $\alpha\beta$-distearin in ether with chlorosulphuric acid, special precautions being taken to avoid contact with water or rise in temperature. The *brucine* salt, obtained by adding brucine dissolved in dry alcohol to the acid ester, forms yellow needles, m. p. 204°, $[\alpha]_D -20{\cdot}49°$ in chloroform. T. A. H.

Electrolysis of the Sodium Salts of Organic Acids. V. JULIUS PETERSEN (*Oversigt K. Danske Vidensk Selsk. Forh.*, 1912, No. 1, 25—47. Compare Abstr., 1900, ii, 522).—In the electrolysis of sodium acrylate in acid solution, the reactions represented by the following equations take place:

(1) $2CH_2{:}CH{\cdot}CO_2H = 2CH_2{:}CH{\cdot}CO_2{\cdot} + H_2$.
(2) $2CH_2{:}CH{\cdot}CO_2{\cdot} + H_2O = 2CH_2{:}CH{\cdot}CO_2H + O$.
(3) $2CH_2{:}CH{\cdot}CO_2{\cdot} = CH_2{:}CH{\cdot}CO_2H + CH{\vdots}CH + CO_2$.

(1) and (2) are the chief reactions, (3) being only subsidiary. The formation of acetylene was observed whether the solution was acid, neutral, or alkaline. Carbon monoxide was also formed in small quantity, according to the equation: $2C_2H_2 + 3O_2 = 4CO + 2H_2O$. Experiments on a larger scale to test whether the reaction: $2CH_2{:}CH{\cdot}CO_2{\cdot} = CH_2{:}CH{\cdot}CH{:}CH_2 + 2CO_2$ takes place, which reaction would be similar to that occurring in the electrolysis of salts of fatty acids, indicated that not divinyl, but a little ethylene was produced. This ethylene may have been formed by the reduction of acetylene, or from propionic acid formed by reduction of some of the acrylic acid. A little acetaldehyde was also formed, probably by the hydration of acetylene.

The reactions taking place on the electrolysis of solutions of potassium crotonate are similar to (1), (2), and (3) given above, the hydrocarbon produced being allylene. Some acetone is also formed by the addition of water to the allylene, and the solution contains an aldehyde, probably propaldehyde.

The chief reaction occurring in the electrolysis of solutions of potassium undecenoate is the formation of the diolefine, $C_{10}H_{19}{\cdot}C_{10}H_{19}$, according to the equation: $2C_{10}H_{19}{\cdot}COO{\cdot} = C_{10}H_{19}{\cdot}C_{10}H_{19} + 2CO_2$. This reaction is thus analogous to that occurring in the electrolysis of salts of the fatty acids. The acetylene hydrocarbon, $C_{10}H_{18}$, is also formed according to reaction (3), and this, by the addition of water,

gives rise to a mixture of the primary and secondary unsaturated alcohols, $C_{10}H_{19}\cdot OH$. The amount of oxygen evolved during the electrolysis is vanishingly small.

The electrolysis of solutions of potassium oleate gave results similar to those obtained with potassium undecenoate, the chief product being the diolefine, $C_{17}H_{33}\cdot C_{17}H_{33}$. The accompanying products were the acetylene hydrocarbon, $C_{17}H_{32}$, and a mixture of the unsaturated alcohols, $C_{17}H_{33}\cdot OH$. T. S. P.

Acyclic Aldehydes. Succinic Semi-aldehyde [β-Aldehydopropionic Acid]. E. CARRIÈRE (*Compt. rend.*, 1912, **154**, 1173—1175).—Harries and Alefeld (Abstr., 1909, i, 132, 133) prepared β-aldehydopropionic acid by decomposing allylacetic acid ozonide with water, but according to the present author the product was not pure. The substance is best prepared by hydrolysing ethyl monoformylsuccinate with oxalic acid in aqueous solution. As thus obtained, it is a liquid, b. p. 142—153°/15 mm., which changes spontaneously into a polymeride, m. p. 167°; molecular weight determinations show that this substance is termolecular and not bimolecular, as stated by Harries and Alefeld. On distillation in a vacuum, the solid furnishes β-aldehydopropionic acid, whilst the residue is a *compound*, m. p. 146°, resulting from the elimination of $1H_2O$ from two molecules of the aldehyde.

Unimolecular β-aldehydopropionic acid gives a semicarbazone, m. p. 194—195° (decomp.), a *p*-nitrophenylhydrazone, m. p. 180—181°, an *oxime*, m. p. 102—103, and a *compound* with pyruvic acid and β-naphthylamine, m. p. above 250°. The foregoing boiling and melting points are considerably higher than those given by Harries and Alefeld.

The possibility of the aldehyde having a lactonic structure appears to be excluded by the fact that on esterification with ethyl alcohol it yields an *ester*, b. p. 84°/12 mm., and an *acetal*, b. p. 105°/12 mm. The ester alone is obtained on esterifying the polymeride; it forms a crystalline *semicarbazone*, a p-*nitrophenylhydrazone*, and an *oxime*, b. p. 139°/14 mm. Hydrazine hydrate gives a *compound*, m. p. 37°, b. p. 145°/19 mm. W. O. W.

Synthesis by means of Mixed Organo-metallic Zinc Derivatives. Aldehydes. EDMOND É. BLAISE (*Compt. rend.*, 1912, **154**, 1086—1088. Compare Abstr., 1911, i, 175, 260).—Hydrolysis of the *cyclo*acetals described in a previous communication (this vol., i, 236) leads to the formation of aldehydes in accordance with the equation

$CHR{<}{{CO\cdot O}\atop{O}}{>}CHMe + H_2O = CH_3\cdot CH(OH)\cdot CO_2H + R\cdot CHO$. The yields are moderately good.

a-Formoxypropionic acid crystallises in needles, m. p. 78°, b. p. 120—121°/13 mm.; the *chloride*, b. p. 59°/10 mm., gives an *anilide*, m. p. 82°, and on treatment with zinc *n*-propyl iodide yields the normal cyclo*acetal* of lactic acid, b. p. 82°/17 mm., together with the cyclo*acetal*, $CHMe{<}{{CO\cdot O}\atop{O}}{>}CHMe$, the latter arising by elimination of 3CO and 2HO from 2 mols. of the acid chloride.

*Formoxy*iso*butyric acid* occurs in needles, m. p. 64—65°, b. p.

125—126°/15 mm.; the *chloride* has b. p. 53·5—54°/14 mm., and the *anilide*, m. p. 100—101°. Treatment of the acid chloride with zinc *n*-propyl iodide gives the corresponding cyclo*acetal*, b. p. 84—85°/20 mm. On boiling with aqueous oxalic acid an 80% yield of butaldehyde is obtained. W. O. W.

cis-trans-Camphoramide, Chlorocyanocamphoric Acid, and Camphoronitrile. JULIUS BREDT (*Ber.*, 1912, 45, 1419—1429).—[With S. LINCK and M. DE SOUZA.]—The camphoramide, obtained by Winzer from ethyl camphorylmalonate and ammonia (Abstr., 1890, 1150), is the *cis*-compound, since it yields *cis*-camphoric acid by treatment with nitrous acid.

By the action of saturated aqueous ammonia at 0° on *cis*-camphoryl chloride, the authors have obtained *sec*-cyanocamphoric acid (the formation of which indicates that *cis*-camphoryl chloride has the asymmetric constitution, $C_8H_{14}<{CCl_2 \atop -CO-}>O$) and a *substance*,

$$C_{10}H_{18}O_2N_2,H_2O,$$

m. p. 132° (decomp.) (160° when anhydrous), which is shown to be cis-trans-*camphoramide* by its conversion into *cis-trans*-camphoric acid by nitrous acid. By treatment with bromine and potassium hydroxide it yields a *substance*, m. p. 158—159°, which contains bromine, whereas Winzer's amide yields a carbamide under these conditions (Errera, Abstr., 1905, i, 383). Both camphoramides yield camphorimide when boiled with alcoholic potassium hydroxide. When *cis-trans*-camphoryl chloride is treated with saturated aqueous ammonia at 0°, a cyanocamphoric acid is not formed, the hydrated *cis-trans*-camphoramide alone being produced.

[With AUG. AMAN.]—Chlorocamphoryl chloride reacts with 11·6% aqueous ammonia at 0° to form *chloro*-sec-*cyanocamphoric acid*,

$$\begin{matrix} CH_2\cdot CCl(CN) \\ | \\ CH_2\cdot CMe(CO_2H) \end{matrix} > CMe_2,$$

m. p. above 250° (decomp.), large, flat prisms, which is converted into camphanonitrile by warm aqueous sodium carbonate.

[With M. DE SOUZA.]—sec-*Cyanocamphoramide*,

$$\begin{matrix} CH_2\cdot CH(CN) \\ | \\ CH_2\cdot CMe(CO\cdot NH_2) \end{matrix} > CMe_2,$$

m. p. 130°, long needles, obtained by heating *sec*-cyanocamphoric acid with phosphorus pentachloride in petroleum (low b. p.), removing the solvent and the phosphoryl chloride produced, and treating the residue with saturated, aqueous ammonia at 0°, is converted into *camphoronitrile*, $C_8H_{14}<{CN \atop CN}$, m. p. 160°, by heating with phosphorus pentachloride on the water-bath. C. S.

Existence of Liquid Racemates. J. GRÓH (*Ber.*, 1912, 45, 1441—1447).—The problem whether fused methyl racemate exists as such or as a mixture of the tartrates has been attacked by measuring the velocity of crystallisation, the temperature-coefficient of the molecular surface-energy, the molecular heat of vaporisation, and by

Nernst's partition method. The last method proves unsuitable with the substance in question; the other methods prove, although not conclusively, that methyl racemate exists in the liquid state as a mixture of the tartrates. C. S.

Preparation of Glutaric Acid by Knoevenagel's Method. HENRI GAULT (*Bull. Soc. chim.*, 1912, [iv], **11**, 380—382).—The improvement suggested consists in using 4 mols. of ethyl malonate to 2 mols. of formaldehyde in place of 2 mols. of the ester as used by Knoevenagel (Abstr., 1894, i, 570). The mixture is cooled in melting ice, 1 to 1·5 grams of piperidine or diethylamine added, and the whole set aside during eighteen to twenty-four hours with frequent agitation. The mixture is then extracted with ether and the residue, left on distilling off the ether, fractionally distilled. Under these conditions the yield of ethyl methylenedimalonate is 81 to 82% with small amounts of ethyl pentanehexacarboxylate, and no ethyl methylenemalonate (compare Bottomley and Perkin, Trans., 1900, **77**, 294). Ethyl methylenedimalonate on boiling with diluted hydrochloric acid gives a quantitative yield of glutaric acid. T. A. H.

Dibasic Ketonic Acids. α-Ketoadipic Acid. HENRI GAULT (*Bull. Soc. chim.*, 1912, [iv], **11**, 382—389. Compare Blaise and Gault, Abstr., 1911, i, 520, 664; Gault, this vol., i, 237).—A more detailed account of work already published (Abstr., 1909, i, 362). Ethyl α-oxalylglutarate, $CO_2Et{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO{\cdot}CO_2Et){\cdot}CO_2Et$, yields a *phenylhydrazone*, m. p. 114—115°, and a *semicarbazone*, m. p. 128°. On hydrolysis by boiling diluted hydrochloric acid, the ester yields α-ketoadipic acid, $CO_2H{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO_2H$, m. p. 126—127°, which separates anhydrous from ether or alcohol, but sometimes as an unstable *hydrate*, m. p. 90—95° (approx.) from water. The salts are difficult to prepare. The *phenylhydrazone*, m. p. 141°, forms small, pale yellow crystals from dilute alcohol; the *semicarbazone* has m. p. 210—215° (approx.), and is sparingly soluble; the oxime, m. p. 151—152°, has been obtained already by Dieckmann (Abstr., 1900, i, 297). The *ethyl* ester, b. p. 148°/9 mm. or 157°/16 mm., is a colourless liquid, giving a *phenylhydrazone*, m. p. 77°, crystallising from dilute alcohol in yellow needles, and a *semicarbazone*, m. p. 118°, forming colourless leaflets from warm water. Under the influence of sodium ethoxide, ethyl α-ketoadipate undergoes lactonisation, forming the substance $\begin{array}{l} CO_2Et{\cdot}[CH_2]_3{\cdot}\overset{}{C}O(CO_2Et){\cdot}O \\ CO_2Et{\cdot}[CH_2]_2{\cdot}CH\text{———}CO \end{array}\!\!>\!CO$ (compare Abstr., 1911, i, 709). T. A. H.

Citrophosphate Solutions. UGO PRATOLONGO (*Atti R. Accad. Lincei*, 1912, [v], **21**, i, 363—364).—A reply to Quartaroli (this vol., i, 238). R. V. S.

Condensation by means of Ultraviolet Light. RICHARD PRIBRAM and ADOLF FRANKE (*Monatsh.*, 1912, **33**, 415—439).—The authors have confirmed their previous conclusion (Abstr., 1911, i, 420) that purified formaldehyde in aqueous solution when exposed to

ultraviolet light yields glycollaldehyde, the identity of which was proved by reducing it to ethylene glycol by means of aluminium amalgam. Control experiments showed that ethylene glycol is not produced in this manner in a solution of formaldehyde which has not been exposed to ultraviolet light. In addition higher condensation products are formed together with formic acid. The oxygen necessary for the production of the latter compound is not obtained from the water present, since the latter, under the experimental conditions chosen, is shown to suffer no decompositiom; neither can it come from the air, since formic acid is still produced when air is completely excluded. It appears probable that a type of Cannizzaro reaction occurs, in which formaldehyde, under the influence of ultraviolet light, becomes decomposed into formic acid and methyl alcohol. The presence of the latter could not be proved, possibly owing to its reconversion into formaldehyde with liberation of hydrogen, which, however, is only partly evolved.

The condensation of formaldehyde is accompanied by slight decomposition, whereby carbon dioxide, carbon monoxide, hydrogen, and methane are formed. H. W.

The Polymerisation of Certain Aldehydes of the Series $C_nH_{2n}O$. ADOLF FRANKE and HERMANN WOZELKA (*Monatsh.*, 1912, **33**, 349—362).—The polymerisation products of *n*-butaldehyde, heptaldehyde, and of the so-called *i*-valeraldehyde have been studied.

When cooled dry hydrogen chloride is passed into *n*-butaldehyde cooled to $-20°$ until the temperature begins to rise, the aldehyde, after some time, becomes viscous and deposits slender needles of n-*metabutaldehyde*, which can be separated from the oily n-*parabutaldehyde*. The latter, on distillation, leaves a small residue of aldehyde resin, and is obtained as a colourless oil, b. p. 105—108°/12 mm., which does not solidify at $-20°$. When distilled under ordinary pressure, it yields the unimolecular aldehyde and aldehyde resin. Its molecular weight, determined in benzene solution and also by the Bleier-Kohn method, corresponds with the formula $(C_4H_8O)_3$. When treated with a minute quantity of sulphuric acid and distilled, it yields the unimolecular aldehyde, together with a small quantity of an oil, b. p. 166—176°, M.W. 117° (compare Gorrhan, Abstr., 1905, i, 171,). Depolymerisation is more readily accomplished by the use of a trace of hydrochloric acid. *n*-Metabutaldehyde separates from ether in long needles, m. p. 173°. It is stable at ordinary temperatures and sublimes at 150°. Determination of its molecular weight in benzene solution gives values intermediate between those required by the formulæ $(C_4H_8O)_3$ and $(C_4H_8O)_4$. When heated at 200°, it forms the unimolecular aldehyde and its condensation products. Depolymerisation occurs more readily in the presence of a trace of acid.

Polymerisation of *n*-butaldehyde could also be brought about by sulphuric acid.

Heptaldehyde, when similarly treated, gives a small quantity of crystals of *metaheptaldehyde*, and an oil which, on distillation under diminished pressure, yields unchanged heptaldehyde, a fraction of indefinite b. p., *paraheptaldehyde*, b. p. 200—203°/12 mm., and alde-

hyde resin. Paraheptaldehyde is a colourless, viscous liquid, which, when cooled, solidifies to a fat-like mass, m. p. 20°. When preserved for some time or distilled, it yields unimolecular heptaldehyde and its condensation products as well as aldehyde resin. The molecular weight, determined in benzene solution, agreed with the formula $C_{21}H_{42}O_3$. Concentrated hydrochloric acid caused complete depolymerisation into the unimolecular aldehyde. Metaheptaldehyde forms long, silky needles, m. p. 140°. For its molecular weight in benzene solution, values were found intermediate between those required by the formulæ $(C_7H_{14}O)_3$ and $(C_7H_{14}O)_4$. Depolymerisation occurs at 200°.

i-Valeraldehyde, a mixture of *i*-propylacetaldehyde and active methylethylacetaldehyde, obtained by the oxidation of commercial active amyl alcohol, has α +3·60° (l = 100). When treated as above with hydrogen chloride, polymerisation occurs, but without formation of metavaleraldehyde. The oily product yields mainly *paravaleraldehyde*, b. p. 122—124°/10 mm., and aldehyde resin. The former is a colourless oil, which solidifies below −5°. Its molecular weight, determined in benzene solution, corresponds with the formula $C_{15}H_{30}O_3$. Depolymerisation is readily effected by concentrated sulphuric acid, only a small quantity of resin being simultaneously formed.

Attempts were made to separate the two aldehydes by taking advantage of a possible difference in their velocities of polymerisation under the influence of hydrogen chloride. In these circumstances, *i*-valeraldehyde, α_D +3·60°, yields an unpolymerised aldehyde, α_D +1·23°. The polymerised portion was, however, found to be inactive, but on depolymerisation by means of a trace of hydrochloric acid gave a unimolecular aldehyde, α_D +1·78°, which became inactive when preserved during six weeks in a vacuum. A second portion of the polymerised aldehyde was similarly preserved, and, after distillation, was also found to be inactive. Depolymerisation, however, yielded an active unimolecular aldehyde, α_D −0·66°. This activity disappeared after fourteen days. A specimen of paravaleraldehyde was preserved during eight months, at the end of which it had become partly depolymerised. Both polymerised and depolymerised aldehyde are inactive, but depolymerisation of the former by means of concentrated sulphuric acid gives a unimolecular aldehyde, α_D +0·1°.

H. W.

Preparation of Methyleneacetone [Δ^{α}-Buten-γ-one] and its Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 242612).—*Δ^{α}-Buten-γ-one*, COMe·CH:CH$_2$, a colourless liquid, b. p. 80° with unpleasant odour and of therapeutic value, is prepared either by distilling β-acetylacrylic acid, COMe·CH:CH·CO$_2$H, at 80—120°, or by heating it with water under pressure. In a similar manner *β-methylacetylacrylic acid,* COMe·CMe:CH·CO$_2$H (prepared by elimination of hydrogen bromide from bromomethyl-lævulic acid, CH$_3$·CO·CBrMe·CH$_2$·CO$_2$H), on distillation furnishes *methylene-ethylmethyl ketone* [*β-methyl-Δ^{α}-buten-γ-one*], COMe·CMe:CH$_2$, a colourless oil, with similar properties and b. p. 96°. F. M. G. M.

Syntheses Starting from Butyrone. GAËTAN AMOUROUX and MARCEL MURAT (*Compt. rend.*, 1912, **154**, 992—994).—Pure

butyrone has b. p. 144—145°/760 mm., D^0 0·8195, n_D 1·414. When treated with magnesium *iso*amyl bromide, it yields *dipropyl*iso*amylcarbinol*, b. p. 114—116°/17 mm., D^0 0·8548, D^{19} 0·8388, n_D 1·443; when the carbinol is passed over alumina at 300°, the unsaturated *hydrocarbon*, $C_{12}H_{24}$, b. p. 190—191°/760 mm., is obtained. The corresponding saturated *hydrocarbon*, $C_{12}H_{26}$, obtained by the catalytic method has b. p. 189°/760 mm., D^{14} 0·7538.

Butyrone and magnesium *iso*butyl chloride react, giving a 20% yield of *dipropyl*iso*butylcarbinol*, b. p. 112—114°/20 mm., D^0 0·8577, D^{14} 0·8445, n_D 1·439; the unsaturated *hydrocarbon*, $C_{11}H_{22}$, has b. p. 180—183°/760 mm.

Butyrone and magnesium phenyl bromide yield *phenyldipropylcarbinol*, b. p. 134°/26 mm., D^0 0·9589, D^{15} 0·9470, n_D 1·516; the *acetate* has b. p. 160°/19 mm. (slight decomp.). *Phenylpropylbutylene* has b. p. 228°/760 mm., and yields a *nitrosochloride*, m. p. 112° (decomp.).

Benzyldipropylcarbinol, b. p. 161—163°/30 mm., D^0 0·9506, n_D 1·513, forms an unsaturated *hydrocarbon*, $C_{14}H_{20}$, b. p. 246—248°/760 mm., D^{19} 0·902 (*nitrosochloride*, m. p. 115°); hydrogenation in presence of nickel gives δ-*benzylheptane*, b. p. 241—243°/756 mm., D^{14} 0·854. Magnesium *cyclo*hexyl chloride and butyrone furnish cyclo*hexyldipropylcarbinol*, b. p. 128—130°/11 mm., D^0 0·9157, D^{19} 0·9025, n_D 1·469. The unsaturated *hydrocarbon*, $C_{13}H_{25}$, b. p. 226—228°/755 mm., D^{21} 0·8441, gives a *nitrosochloride*, m. p. 110° (decomp.), and on hydrogenation yields δ-cyclo*hexylheptane*, b. p. 228°/760 mm. W. O. W.

Reduction of β-Diketones. ÉDOUARD BAUER (*Compt. rend.*, 1912, **154**, 1092—1094).—Acetylacetone (60 grams) may be reduced to βδ-dihydroxypentane by treatment with absolute alcohol (450 grams) and sodium (100 grams) until the latter is dissolved. Under these conditions benzoylacetone gives the aldol, $OH\cdot CMe_2\cdot CH_2Ac$, together with γ-hydroxy-α-phenylbutane and the corresponding glycol. Dibenzoylmethane likewise yields α-hydroxy-βγ-diphenylpropane and a *product*, b. p. 199—202°/13 mm., containing C 84·4, H 7·27%.

W. O. W.

Compounds of Carbohydrate Derivatives with Magnesium Methyl Iodide. EMIL FISCHER and KURT HESS (*Ber.*, 1912, **45**, 912—915).—Acetobromoglucose reacts with magnesium methyl iodide, forming a colourless, amorphous insoluble additive product,

$$C_{14}H_{19}O_9Br,2MgCH_3I.$$

Water decomposes it with the formation of acetobromoglucose; alcohols, for example, methyl alcohol, give rises to methyl glucoside. Penta-acetylglucose, tetra-acetylglucose, and tetra-acetyl methylglucoside also form similar additive products with two molecules of magnesium methyl iodide. E. F. A.

Esters and Amides of Phosphoric Acid. III. Dihydroxyacetone- and Lævulose-phosphoric Acids. KURT LANGHELD (*Ber.*, 1912, **45**, 1125—1127).—Dihydroxyacetone dissolved in water was evaporated in a vacuum to a syrup and treated with ethyl metaphosphate

(less than 1 mol.). On cooling, the mixture solidified to a white mass, which was treated with chloroform to remove unchanged ester, and the residue dissolved in water and neutralised with barium hydroxide. After filtering off any barium phosphate, alcohol was added, and the *barium dihydroxyacetone-phosphate* separated as a white, amorphous compound, $C_3H_5O_6PBa$, which became crystalline after a time. The salt reduced Fehling's solution and silver nitrate, and gave with phenylhydrazine an *osazone* containing phosphorus and melting at 143°.

Barium laevulose-phosphate, $C_6H_{11}O_9PBa,H_2O$, was obtained from lævulose in a similar manner. It was a crystalline compound, reduced Fehling's solution on warming, and yielded a *phenylosazone*, $C_{18}H_{23}O_7N_4P$, melting at 158°. These salts appear to be different from those obtained by Neuberg (Abstr., 1910, i, 610), in that the salts are crystalline and form osazones. Barium salts corresponding with diphosphoric esters of dihydroxyacetone and lævulose were obtained when excess of ethyl metaphosphate was employed.

Analysis of the lævulose compound agreed with the composition $C_6H_{10}O_{12}P_2Ba_2,H_2O$. W. J. Y.

Crystallographic Notes on Inosite, Potassium Nitrate, and Carbamide Nitrate. THOMAS VIPOND BARKER (*Min. Mag.*, 1912, 16, 207—216).—New crystal-forms are noted on inosite, and a new orientation of the crystals is suggested. The rhombohedral modification of potassium nitrate fails to give a parallel growth on calcite.

Carbamide nitrate has the ratios $a:b:c=0{\cdot}9965:1:0{\cdot}9142$; $\beta=75°2\frac{1}{2}'$. Crystals of the salt immersed in a saturated solution show marked differences in relief under the microscope, since the refractive index α is approximately the same as that of the liquid, whilst γ is considerably higher. L. J. S.

Cellulose. III. Xyloidins. H. JENTGEN (*Zeitsch. angew. Chem.*, 1912, 25, 944—947).—It is proposed to classify under the group name "xyloidins," all substances formed by dissolving cellulose in nitric acid which are precipitated as amorphous masses from these solutions by water.

An account is given of a number of experiments dealing with the behaviour of different forms of cellulose (cotton wool, cotton waste, etc.) towards nitric acid of densities varying from 1·460 to 1·500.

The solution which first results from the action of nitric acid on cellulose is fairly viscous, but within twenty-four hours the viscosity falls, until it is about equal to that of water. In no case was it found possible to completely dissolve the cellulose in nitric acid; a few fibres always remained undissolved.

The results recorded show that the percentage of nitrogen in the product increases as the strength of the nitric acid employed in its preparation becomes greater, ranging from 6·2% to 11·0%. Similarly, the xyloidin becomes more readily soluble as the strength of the nitric acid is increased; thus, the nitrate obtained by the action of nitric acid (D 1·465) on cellulose is not affected by cold glacial acetic acid, but dissolves in the hot solvent, separating from the solution again when cold, whilst the nitrate resulting from the action of nitric acid

(D 1·470) swells up when brought into contact with cold glacial acetic acid, dissolves in the solvent when heated, and does not separate from the solution when cold. The products of the action of nitric acid of higher concentrations are readily soluble in acetic acid and acetic anhydride, whilst the higher nitrated products are soluble in most solvents.

The xyloidins decompose at 196—197°, and burn quite quietly when ignited; they contain from 2·5 to 4·0% of hygroscopic water, and, unlike collodion wool, become yellow to greenish-yellow when treated with potassium iodide. The xyloidins also differ from gun-cotton and collodion wool, in that they are much more readily attacked by hydrochloric acid, being converted in a few hours into acid-celluloses.

W. H. G.

Mirror Image Isomerism with Chromium Compounds. II. ALFRED WERNER (*Ber.*, 1912, **45**, 865—869. Compare Abstr., 1911, i, 951).—The author has succeeded in resolving triethylenediaminechromium salts into their optically active isomerides. Resolution by means of the tartrates, chloride and bromide tartrates, bromocamphorsulphonates, or camphorsulphonates was not successful, since the aqueous solutions of the salts are so sensitive that they undergo change even on evaporation; as a rule, the yellow colour changes to violet, and triethylenediamine salts can no longer be obtained from the solution.

The salts formed with nitrocamphor, and which the author designates as camphornitronates, were found to resolve readily into their optical isomerides, *d*-triethylenediaminechromium *d*-camphornitronate being very sparingly soluble in water, whilst the corresponding *dl*-isomeride is readily soluble. No partial racemate is formed between the isomerides.

The resolution is carried out as follows: To a solution of 6 grams of triethylenediaminechromium chloride, $[Cr\ en_3]Cl_3,3\frac{1}{2}H_2O$, in 20 c.c. of water is added a solution of 6 grams of sodium *d*-camphornitronate in 15 c.c. of water. The sparingly soluble d-*triethylenediaminechromium* d-*camphornitronate* immediately separates as a light yellow, powdery precipitate. After collecting the precipitate, further addition of sodium camphornitronate to the mother liquor produces, after two hours, another crop of small, yellow crystals. The mother liquor then contains the *l*-triethylenediaminechromium *d*-camphorsulphonate.

d-*Triethylenediaminechromium iodide*, $[Cr\ en_3]I_3,H_2O$, is obtained by triturating a thin aqueous paste of the *d*-camphornitronate with sufficient solid sodium iodide to cause it to set to a dark yellow mass. After washing this mass with a little water, alcohol and ether, it can be purified by re-precipitation from a concentrated aqueous solution of sodium iodide. It forms golden-yellow, flat, glistening crystals, and has $[a]_D$ +60°, $[M]_D$ +378·67°. The l-*iodide*,

$$[Cr\ en_3]I_3,H_2O,$$

is obtained from the mother liquor from the *dd*-camphornitronate as follows: The addition of 5 grams of sodium iodide to the mother liquor gives a precipitate of an inactive iodide; after collecting this, the further addition of 8 grams of sodium iodide precipitates the active

l-iodide, which resembles the *d*-isomeride in appearance; $[a]_D$ $-60°$, $[M]_D$ $-378·67°$.

The d-*thiocyanate*, $[Cr\ en_3](SCN)_3,H_2O$, was obtained from a concentrated solution of the *d*-iodide by precipitation with solid potassium thiocyanate. It is a yellow, crystalline powder, and has $[a]_D$ $+78°$, $[M]_D$ $+330·72°$. The l-*thiocyanate*, $[Cr\ en_3](SCN)_3,H_2O$, was prepared similarly, from the *l*-iodide, and has $[a]_D$ $-80°$, $[M]_D$ $-339·2°$.

The racemic iodides and thiocyanates have the same composition as the active isomerides. T. S. P.

Mirror-Image Isomerism with Rhodium Compounds. I. ALFRED WERNER (*Ber.*, 1912, 45, 1228—1236).—The similarity between the compounds of rhodium and cobalt (compare Abstr., 1906, i, 450) would indicate that triethylenediaminerhodium salts should form optical isomerides, as is the case with the corresponding cobalt compounds (this vol., i, 166). As a matter of fact the author has been successful in carrying out the resolution of the rhodium salts. Starting with triethylenediaminerhodium chloride, it was found that by precipitation with sodium camphornitronate (compare preceding abstract) the sparingly soluble *l*-triethylenediaminerhodium camphornitronate was obtained, the *d*-isomeride remaining in solution. An alternative method of resolution was to prepare a solution of the chloride tartrate from the chloride by interaction with silver tartrate. On concentration, the *l*-triethylenediaminerhodium chloride tartrate first separated in transparent, glistening crystals, the corresponding *d*-isomeride separating later as non-transparent, fibrous crystals. From the above compounds the various active salts could be obtained.

The active isomerides are very stable; their aqueous solutions can be evaporated down without loss of activity. They are also quite stable towards acids. It is noteworthy that the rotatory power of the rhodium compounds is of the opposite sign to that of the cobalt and chromium compounds, and from a consideration of the various active compounds which have been prepared, the author draws the conclusion that those asymmetric isomerides have corresponding configurations which give the more sparingly soluble salts with the same active acid. Cobalt and chromium give sparingly soluble *d*-isomerides, whilst rhodium gives sparingly soluble *l*-isomerides, so that rhodium has an optical effect exactly opposite to that of cobalt and chromium. Comparison of the rotatory powers of the triethylenediamine-rhodium and -chromium salts shows that they are of the same order; the rotation dispersion of rhodium salts is, however, very small, so that white light can be used in the optical measurements.

The present results, together with those previously obtained, indicate that the nature of the central atom is of decisive importance in determining the direction of rotation.

Triethylenediaminerhodium chloride, $YCl_3,2\frac{1}{2}H_2O$, where $Y=[Rh\ en_3]$, was obtained in the impure condition by the interaction of 45 grams of ethylenediamine monohydrate with 100 grams of sodium rhodichloride. Repeated crystallisation from water does not free it from sodium chloride, with which it is isomorphous. The pure chloride is

obtained from the iodide by shaking a solution with excess of freshly precipitated silver chloride. It forms transparent, cubical crystals or small, glistening needles, and loses $2\frac{1}{2}H_2O$ at 120°. The *iodide*, $YI_3,\frac{1}{2}H_2O$, was prepared from the impure chloride by precipitation with sodium iodide, and crystallises in transparent, rhombohedral crystals.

l-*Triethylenediaminerhodium camphornitronate* was obtained as a sparingly soluble precipitate by the interaction of 5 grams of the chloride with 4 grams of sodium camphornitronate in aqueous solution. When rubbed to a thin paste with water and solid sodium iodide, the l-*iodide*, $YI_3,\frac{1}{2}H_2O$, separated, and could be extracted with water and recrystallised. It crystallises in small, glistening cubes, and has $[\alpha]_D -50°$, $[M]_D -336·5°$.

When the mother liquor from the *l*-camphornitronate was precipitated with sodium iodide, a white precipitate, containing chiefly inactive iodide, was formed. The filtrate from this precipitate was evaporated almost to dryness on the water-bath, and the residue extracted with boiling alcohol to remove sodium camphornitronate. The product remaining was dissolved in water and the solution precipitated with solid sodium iodide, whereby the pure d-*iodide*, $YI_3,\frac{1}{2}H_2O$, was obtained in cubical, efflorescent crystals, having $[\alpha]_D +48°$ and $[M]_D +323°$; $[\alpha]_C +40°$, $[M]_C +269·2°$.

The l-*chloride* d-*tartrate*, $YCl(C_4H_4O_6),5H_2O$, was obtained from the *r*-chloride and silver *d*-tartrate in the way already indicated, as was also the d-*chloride* d-*tartrate*, $YCl(C_4H_4O_6),4H_2O$. The former crystallises in transparent, well-defined cubes, and has $[\alpha]_D -50°$, $[M]_D -278·25°$; the latter deposits in the form of spherical crusts, and has $[\alpha]_D +44°$ and $[M]_D$ 244·86°. The *l*-iodide is readily obtained from the *l*-chloride *d*-tartrate by precipitation with sodium iodide, as also is the *d*-iodide from the *d*-chloride *d*-tartrate; in the latter case, however, fractional precipitation must be resorted to, since the inactive iodide is first deposited.

The l-*chloride*, $YCl_3,2\frac{1}{2}H_2O$, was prepared from the *l*-iodide by a method similar to that used for obtaining the pure inactive chloride. It crystallises in long, white, efflorescent needles, and has $[\alpha]_D -80°$, $[M]_D -347·6°$. The d-*chloride* forms similar crystals, and has $[\alpha]_D +78°$, $[M]_D +338·9°$. The l-*thiocyanate*, $Y(SCN)_3$, was obtained from the iodide by double decomposition with potassium thiocyanate. It forms large, dull, lancet-shaped crystals, and has $[\alpha]_D -72°$, $[M]_D -329°$. The d-*thiocyanate* is similar, and has $[\alpha]_D +74°$, $[M]_D +338°$.

T. S. P.

Crystallography of Some New Organic Compounds. EDOARDO BILLOWS (*Zeitsch. Kryst. Min.*, 1912, **50**, 504—509; from *Riv. Min. Crist. Ital.*, 1909, **39**, 3—20).—The compounds of hexamethylenetetramine examined were prepared by G. A. Barbieri. $MgI_2,2C_6N_4H_{12},9H_2O$, monoclinic, $a:b:c=0·8802:1:0·4951$; $\beta=90°1'$. $Mg(NO_3)_2,2C_6N_4H_{12},10H_2O$, orthorhombic, $a:b:c=0·8261:1:0·4813$. $Mn(NO_3)_2,2C_6N_4H_{12},10H_2O$, orthorhombic, $a:b:c=0·8388:1:0·4894$. $2Mg(NO_2)_2,3C_6N_4H_{12},25H_2O$, triclinic, $a:b:c=0·8461:1:0·8460$; $\alpha=126°5'$, $\beta=49°10'$, $\gamma=121°15'$.

$MgCl_2,2C_6N_4H_{12},9H_2O$, triclinic, $a:b:c=0·8321:1:0·8573$; $\alpha=125°43'$, $\beta=50°21'$, $\gamma=123°56'$. $MgBr_2,2C_6N_4H_{12},9H_2O$, monoclinic, $a:b:c=0·9022:1:0·5111$; $\beta=90°40'$. $Mg(CNS)_2,2C_6N_4H_{12},9H_2O$, triclinic, $a:b:c=0·9342:1:0·9233$; $\alpha=134°12'$, $\beta=47°4'$ $\gamma=120°56'$. $Mn(CNS)_2,2C_6N_4H_{12},4H_2O$, tetragonal, $a:c=1:1·0366$. $Co(CNS)_2,C_6N_4H_{12},4H_2O$, triclinic, $a:b:c=1·4232:1:1·6034$; $\alpha=128°23'$, $\beta=31°6'$, $\gamma=123°33'$. $Ni(CNS)_2,C_6N_4H_{12},4H_2O$, triclinic. Mixed crystals of the last two compounds are also triclinic.

$Fe(CNS)_2,C_6N_4H_{12},4H_2O$, triclinic, $a:b:c=1·4012:1:1·5723$; $\alpha=124°57'$, $\beta=29°54'$, $\gamma=121°36'$. $Er(NO_3)_3,2C_6N_4H_{12},10H_2O$, monoclinic $a:b:c=1·1501:1:1·4892$; $\beta=123°0'$.

$Nd(NO_3)_3,2C_6N_4H_{12},8H_2O$,

monoclinic, $a:b:c=0·7336:1:0·4329$; $\beta=122°30\frac{1}{2}'$.

$NdCl_3,2C_6N_4H_{12},14H_2O$, triclinic. L. J. S.

Walden's Inversion. EINAR BIILMANN (*Annalen*, 1912, **388**, 330—344).—A theoretical paper in which the author points out that the explanations of Walden's inversion, recently advanced by Fischer (Abstr., 1911, i, 418) and by Werner (*ibid.*, 424), and regarded by these authors as very similar to one another, are in reality so different that Fischer's explanation is not an explanation, whilst Werner's hypothesis presents a conception of the mechanism of the change which opens up entirely new possibilities.

The author's objections to Fischer's explanation are twofold. Taking as an example the reaction between ammonia and α-bromopropionic acid, the explanation requires the splitting of the ammonia into hydrogen and the amino-group, and is, therefore, inapplicable in the case of the reaction between an organic halogen compound and a tertiary amine. The second objection is connected with the movements of the other atoms or groups in the molecule after the bromine atom has been loosened; if one of these atoms or groups moves into the place previously occupied by the halogen atom, the effect can be, in the author's opinion, at most racemisation, not inversion. C. S.

The Condensation Products of Choral with Acid Amides. FRANZ FEIST (*Ber.*, 1912, **45**, 945—962).—Anhydrochloralurethane and its analogues are shown to have an ether-like structure,

$$O[CH(CCl_3)\cdot NH\cdot COX]_2,$$

instead of the structure $CCl_3\cdot CH{:}N\cdot COX$, previously accepted (compare Moscheles, Abstr., 1891, 1003; Hantzsch, Abstr., 1894, i, 363; Diels and Seib, Abstr., 1909, i, 885; Diels and Gukassianz, Abstr., 1911, i, 24). The new formula contains two asymmetric carbon atoms, and so in the formation of these substances, meso- and racemic isomerides may be expected; isomerides have in some cases been isolated. The substances are neutral, very stable towards acids and towards potassium permanganate, sensitive towards alkalis, and frequently distillable without decomposition. The addition reaction of anhydrochloralurethane with sodium alcoholate (Diels and Seib, *loc. cit.*) is in reality a scission:

$$\begin{matrix} CCl_3\cdot CH\cdot NH\cdot CO_2Et \\ >O \\ CCl_3\cdot CH\cdot NH\cdot CO_2Et \end{matrix} + NaOMe \longrightarrow \begin{matrix} CCl_3\cdot CH(OMe)\cdot NH\cdot CO_2Et \\ + \\ CCl_3\cdot CH(ONa)\cdot NH\cdot CO_2Et. \end{matrix}$$

Chloralurethane, $CCl_3·CH(OH)·NH·CO_2Et$, is converted into anhydrochloralurethane by treatment with cold sodium hydroxide solution and acetic anhydride; the product has m. p. 149—150°, but is very easily converted by acids into an *isomeride*, m. p. 161—162°; the reverse change is caused by sodium hydroxide. Anhydrochloralurethane can be distilled (b. p. 178°/25 mm., with slight decomp.); phosphorus pentachloride converts it into chloraldiurethane,

$$CCl_3·CH(NH·CO_2Et)_2,$$

m. p. 172°; it does not react with methyl sulphate.

Chloralmethylurethane (from chloral and methyl carbamate) has m. p. 125°; it is dehydrated similarly to the ethyl analogue, giving anhydrochloralmethylurethane, m. p. 173—174°, b. p. 222°/18 mm.; it shows only slight indications of isomerisation. When treated with sodium methoxide solution the anhydro-compound yields *chloralmethylurethane methyl ether*, rectangular plates, m. p. 67°.

*Chloral*isoamylurethane, m. p. 105—106°, was dehydrated to *anhydrochloral*iso*amylurethane*, needles, m. p. 81°, which gave no indication of isomerism.

Chloralmenthylurethane was obtained from the interaction of menthylurethane and chloral in two isomeric forms, m. p. 147—148° and 124—125° respectively; both forms are resolved into their components by heating in a vacuum. It was not possible to obtain the anhydro-compounds.

Chloralformamide, $CCl_3·CH(OH)·NH·COH$, m. p. 118°, obtained by interaction of chloral and formamide, is converted by sodium hydroxide solution and acetic anhydride into anhydrochloralformamide, m. p. 194·5—195°; the *methyl ether* of chloralformamide, obtained by the action of sodium methoxide on the anhydro-compound, forms prisms, m. p. 139°.

Chloralacetamide, m. p. 158—159°, is dehydrated to anhydrochloralacetamide, m. p. 212—213°; the methyl ether,

$$CCl_3·CH(OMe)·NH·COMe,$$

obtained by the action of methyl sulphate on chloralacetamide, and of sodium methoxide on the anhydro-compound, has m. p. 120°.

Chloralbenzamide, m. p. 150°, by dehydration with sodium hydroxide solution and acetic anhydride and subsequent recrystallisation from alcohol yields an *anhydrochloralbenzamide*, m. p. 199—200°, together with the *ethyl ether*, $CCl_3·CH(OEt)·NHBz$, m. p. 144—145°; the latter is also obtainable from the anhydro-compound with sodium ethoxide in the usual way. If the crude anhydride is recrystallised without the use of alcohol there is obtained also the *acetyl* derivative,

$$CCl_3·CH(OAc)·NHBz,$$

m. p. 151°, b. p. 163—165°/25 mm. If the dehydration of chloralbenzamide is effected by sodium hydroxide solution and benzoyl chloride, the product is a mixture of the above anhydro-compound with an *isomeride*, m. p. 138°, together with *benzoylchloralbenzamide*, $CCl_3·CH(OBz)·NHBz$, needles, m. p. 168°. The conversion of the more fusible isomeride into the less fusible is difficult to complete. On heating under reduced pressure, the more fusible isomeride (as also the other isomeride above its m. p.) forms *chloraldibenzamide*, $CCl_3·CH(NHBz)_2$, colourless needles, m. p. 272°; the easy formation of

this substance is a disproof of the structure previously assigned to these anhydro-compounds. The *methyl ether* of chloralbenzamide (m. p. 105—106°, b. p. ca. 200°/22 mm.) is obtainable from the anhydro-compound with sodium methoxide, and from chloralbenzamide itself with methyl sulphate. The *ethyl ether* is described above.

D. F. T.

Derivatives of Monoamino-acids. Picrolonates of Glycine, *d*-Alanine, and *dl*-Leucine. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, **78**, 150—155).—The monoamino-acids form sparingly soluble picrolonates, but these are all so similar as to be useless for the separation of mixtures of amino-acids.

Glycine picrolonate, which is composed of 2 mols. of amino-acid to 1 mol. of picrolonic acid, is prepared by mixing concentrated solutions of the components at the boiling point and heating for a few minutes. It crystallises in lustrous, orange, silky, soft needles, m. p. 208° (corr. decomp.).

The corresponding d-*alanine picrolonate* (2 alanine + 1 picrolonic acid) has m. p. about 145° (decomp.). A second compound (1 alanine + 1 picrolonic acid) has m. p. 215° (decomp 217°), $[\alpha]_D^{20}+11\cdot8°(\pm 0\cdot74°)$.

dl-*Leucine picrolonate* (1 leucine + 1 picrolonic acid) crystallises in long, narrow prisms of greenish-yellow colour, which become yellow when dried, and soften at 130°, m. p. 150° (decomp.).

E. F. A.

Crystalline Form of Some Platinothiocyanates. EDOARDO BILLOWS (*Zeitsch. Kryst. Min.*, 1912, **50**, 509—510; from *Riv. Min. Crist. Ital.*, 1909, **39**, 21—26).—The substances investigated were prepared by A. Minozzi. Potassium platinothiocyanate, $K_2Pt(CNS)_6$, hexagonal holohedral, $a:c=1:0\cdot7829$. Potassium platinothiocyanate dihydrate, $K_2Pt(CNS)_6,2H_2O$, orthorhombic, $a:b:c=0\cdot6224:1:0\cdot9712$. Ammonium platinothiocyanate, $(NH_4)_2Pt(CNS)_6$, hexagonal holohedral, $a:c=1:0\cdot9340$. Sodium platinothiocyanate, $Na_2Pt(CNS)_6,2H_2O$: the microscopic crystals appear to be isomorphous with the corresponding potassium salt. These salts are isomorphous with the corresponding platinoselenocyanates (following abstract).

L. J. S.

Crystallography of Platinoselenocyanates. EDOARDO BILLOWS (*Zeitsch. Kryst. Min.*, 1912, **50**, 494—495; from *Riv. Min. Crist. Ital.*, 1909, **36**, 49—55).—Potassium platinoselenocyanate, $K_2Pt(CNSe)_6$, orthorhombic hemimorphic, $a:b:c=0\cdot5989:1:0\cdot9565$. Potassium platinoselenocyanate dihydrate, $K_2Pt(CNSe)_6,2H_2O$, trigonal scalenohedral, $\rho=38°31\frac{1}{2}'$. Ammonium platinoselenocyanate, $(NH_4)_2Pt(CNSe)_6$, orthorhombic, $a:b:c=0\cdot6338:1:1\cdot0444$.

L. J. S.

Preparation of Bromo-α-ethylbutyrylcarbamide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 243233).—When bromo-α-ethylbutyryl*iso*carbamide methyl ether (this vol., i, 169) is heated with concentrated hydrochloric acid, it evolves methyl chloride and is converted into bromo-α-ethylbutyrylcarbamide:

$$CEt_2Br\cdot CO\cdot NH\cdot C(:NH)\cdot OMe + HCl = CEt_2Br\cdot CO\cdot NH\cdot CO\cdot NH_2 + CH_3Cl.$$

F. M. G. M.

Action of Hydroxycarbamide on Some β-Ketonic Esters. André Meyer (*Compt. rend.*, 1912, **154**, 989—992).—On adding ethyl acetoacetate to an alcoholic solution of hydroxycarbamide, a very soluble additive *compound*, $C_7H_{14}O_5N_2$, m. p. 42—43°, is obtained, together with a *compound*, $C_7H_{12}O_4N_2,0\cdot5H_2O$, crystallising in slender needles, m. p. 45°. Ethyl benzoylacetate in the same way gives by condensation a *compound*, $C_{12}H_{14}O_4N_2$, silky needles, m. p. 98—99°. Ethyl oxalacetate furnishes a *compound*, $C_9H_{14}O_6N_2$, occurring in prisms, m. p. 77°, together with a small quantity of the *compound*, $C_{18}H_{30}O_{13}N_4$, probably a hydrate of the foregoing. W. O. W.

Electrolytic Oxidation of Organic Sulphur Compounds Fritz Fichter and Walter Wenk (*Ber.*, 1912, **45**, 1373—1383).—The authors have extended the observations of Fichter and Sjöstedt (Abstr., 1911, i, 41). In all the experiments, with two exceptions, an anode of platinum gauze was used; in some cases it was not absolutely necessary to use a diaphragm. Except where stated the solvent used was a mixture of glacial acetic acid and concentrated hydrochloric acid,

At 15—20° ethyl thiocyanate is oxidised to ethanesulphonic acid. At 2°, using a current density (*C.D.*) of 0·02 ampere per sq. cm., thiocarbamide is oxidised in hydrochloric acid solution to the compound $S_2[C(NH)\cdot NH_2]_2$ (compare Maly, Abstr., 1890, 1399; Storch, Abstr., 1891, 548), for which the authors adopt the name formamidine disulphide (compare Hector, Abstr., 1892, 292). After electrolysis, the nitrate is readily precipitated from the solution by the addition of potassium nitrate.

Formamidine disulphide sulphate, $C_2H_6N_4S_2,H_2SO_4$, is similarly obtained from thiocarbamide in sulphuric acid ($2N$) solution, using a *C.D.* of 0·01 ampere per sq. cm. In hydrobromic acid solution the corresponding hydrobromide (compare MacGowan, Trans., 1887, **51**, 378) is obtained.

Ethyl sulphide behaves similarly to phenyl sulphide (Fichter and Sjöstedt, *loc. cit.*), ethyl sulphoxide being first formed, and then ethylsulphone. For the preparation of the sulphone it is best first to isolate the sulphoxide.

o-Nitrobenzyl sulphide is readily oxidised to the sulphoxide. The oxidation takes place best in glacial acetic acid-hydrochloric acid solution at 70—75°, using a *C.D.* of 0·06 ampere per sq. cm. If the temperature is raised to 100°, *o*-nitrobenzyl disulphoxide is produced; it is probable that the disulphide is first formed from the sulphoxide (compare Smythe, Trans., 1909, **95**, 349), and then oxidised to the disulphoxide. The production of sulphoxide also takes place when the hydrochloric acid is replaced by phosphoric or nitric acid, but it is then accompanied by some *o*-nitrobenzaldehyde. Oxidation to the sulphone does not take place at platinum anodes. *p*-Nitrobenzyl sulphoxide was obtained similarly from *p*-nitrobenzyl sulphide.

At 10°, with a *C.D.* of 0·02 ampere per sq. cm., acetonediethylmercaptole is oxidised to a mixture of acetone and ethanesulphonic acid. It is probable that the hitherto unknown diethylthionyl-2 : 2-propane, $CMe_2(SOEt)_2$, is first produced, and then decomposed, in the presence of water, by chlorine evolved at the anode from the hydro-

chloric acid in the solvent, according to the scheme: $CMe_2(SOEt)_2 \rightarrow CMe_2Cl_2 + 2Et{\cdot}SO_2Cl \rightarrow COMe_2 + 2Et{\cdot}SO_3H$. This explanation is supported by the fact that when water was excluded from the solvent, which then consisted of glacial acetic acid containing 10% of acetic anhydride and continuously saturated with a current of dry hydrogen chloride, the mercaptol was oxidised to *diethylthionyl*-2 : 2-*propane*, when a graphite anode was used. This compound possesses a most objectionable odour, which is, however, quite different from that of the mercaptole. It is a colourless liquid, heavier than water, and has b. p. 134—135°/14 mm. It is readily reduced to the mercaptole by tin and hydrochloric acid, and oxidised to sulphonal by permanganate in sulphuric acid solution.

Phenyl ethyl sulphide behaves quite differently from the symmetrical sulphides towards electrolytic oxidation, the products being benzenesulphonic acid and acetic acid. It is possible that it is first oxidised to the sulphoxide, but that this unites with hydrogen chloride, loses water, and then decomposes into phenyl mercaptan and acetaldehyde (compare Hilditch, this vol., i, 71), in accordance with the scheme: $SOEtPh \rightarrow OH{\cdot}SEtPhCl \rightarrow SPhCl{:}CHMe \rightarrow PhSH + Me{\cdot}CHO$. The mercaptan and aldehyde are then oxidised to the sulphonic acid and acetic acid. A graphite anode was used in the electrolysis.

At 40—50°, with a *C.D.* of 0·04 ampere per sq. cm., phenyl disulphide is oxidised to two molecules of benzenesulphonic acid, behaving quite differently from benzyl disulphide. When water is excluded and graphite anodes are used, the disulphide is not acted on.

During the course of the investigation, it was found that acetonediethylmercaptole readily gives *additive products* with mercuric nitrate and chloride, having the respective formulæ: $C_7H_{16}S_2,Hg(NO_3)_2$ and $C_7H_{16}S_2,HgCl_2$. The former is insoluble in water, but from alcohol or acetone solution it is obtained as large, thin, flexible tablets with a silver glance; m. p. 76°. The latter is insoluble in water and organic solvents; from concentrated hydrochloric acid solution it is obtained as glistening, white flakelets on the addition of water. When the mercaptole is shaken with a solution of mercurous nitrate, a black precipitate (delicate reaction) is obtained, consisting of mercury and the mercuric nitrate additive product. T. S. P.

Methylated Guanidines. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1912, 77, 328—393. Compare Abstr., 1910, i, 99; 1911, i, 842).—A summary of the subject. Eleven methylated guanidines are possible. Three of these, all containing the grouping $NMe{:}C(NH_2){\cdot}N{:}$, could not be obtained. Attempts to prepare them led to the formation of guanidines with the grouping $NH{:}C(NHMe){\cdot}N{:}$, which appears to be the stable form.

as-Trimethylguanidine, the two tetramethylguanidines, and pentamethylguanidine are prepared for the first time. Other methylguanidines have been obtained by new methods. *s*-$\alpha\beta\gamma$-Trimethylguanidine, $NMe{:}C(NMe)_2$, is formed whenever the conditions are in any way favourable, and in a number of unexpected cases; it is evidently very stable.

Dimethylamine behaves somewhat differently from ammonia or methylamine, carbamide derivatives being obtained with it instead of the methylated guanidines expected.

α-Methylguanidine, $NH:C(NHMe)\cdot NH_2$, forms a *platinichloride*, crystallising in plates, m. p. 194—195°.

γ-Methylguanidine, $NMe:C(NH_2)_2$, could not be prepared.

αα-Dimethylguanidine, $NH:C(NMe_2)\cdot NH_2$, forms an *aurichloride*, crystallising in dark yellow prisms, m. p. 248°, a *platinichloride*, crystallising in needles, m. p. 225°; the picrate has m. p. 230°.

αβ-Dimethylguanidine, $NH:C(NHMe)_2$, may be prepared from methylamine and diethyl iminocarbonate or from methylamine and the methiodide of methylthiocarbamide. The *aurichloride* forms needles and plates, m. p. 122°; the *platinichloride* forms short, thick needles, m. p. 196—197°; the *picrate* gives prisms, m. p. 178°.

This guanidine was also obtained from *s*-dimethylthiocarbamide on treatment with mercury oxide in presence of ammonia, also on heating the ethiodide of *s*-dimethylthiocarbamide with alcoholic ammonia.

αγ-Dimethylguanidine, $NMe:C(NHMe)\cdot NH_2$, could not be obtained.

ααβ-Trimethylguanidine, $NH\cdot C(NMe_2)\cdot NHMe$, prepared by the action of dimethylamine on the methiodide of methylthiocarbamide in sealed tubes at 100° for twelve hours, forms an *aurichloride*, crystallising in needles and thin plates, m. p. 153—155°, and a *platinichloride*, crystallising in needles, m. p. 172—173°.

ααγ-Trimethylguanidine, $NMe:C(NMe_2)\cdot NH_2$, could not be prepared.

αβγ-Trimethylguanidine, $NMe:C(NHMe)_2$, can be obtained by a large variety of methods; the *hydriodide* forms long needles, m. p. above 290°; the aurichloride forms needles, m. p. 156°, and the platinichloride, needles and plates, m. p. 225—226°.

ααββ-Tetramethylguanidine, $NH:C(NMe_2)_2$, prepared by the action of ammonia on the methiodide of tetramethyl thiocarbamide, forms an *aurichloride*, crystallising in slender needles, m. p. 142—144°, a *platinichloride*, crystallising in needles, and a *picrate*, consisting of needles aggregated to form plates, m. p. 130°.

ααβγ-Tetramethylguanidine, $NMe:C(NMe_2)\cdot NHMe$, was obtained on treatment of αβγ-trimethyl-ψ-thiocarbamide with dimethylamine. The *aurichloride* forms needles, m. p. 115—117°; the *picrate* separates in short prisms, m. p. 158—160°.

Pentamethylguanidine, $NMe:C(NMe_2)_2$, was obtained by treating ααβγ-tetramethyl-ψ-thiocarbamide with dimethylamine. Attempts to prepare it from ethyl methyl iminocarbonate and dimethylamine or from ethyl methyl iminodithiocarbonate and dimethylamine were unsuccessful. The *aurichloride* forms slender needles, m. p. 130—132°; the *picrate* separates in long needles, m. p. 160—162°. E. F. A.

The Formation of Triazomethylurethane from Triazoacetic Acid. THEODOR CURTIUS and AUGUST BOCKMÜHL (*Ber.*, 1912, 45, 1033—1036)—An extension of the work of Curtius, Darapsky, and Bockmühl on the hydrazide and azide of triazoacetic acid is here described (compare Abstr., 1908, i, 144). It is found that those

hydrazides which are only obtained as unstable syrups can readily be purified in the form of their condensation products with acetone, any excess of hydrazine hydrate being converted into the easily soluble dimethylketazine (compare the following abstracts). The acetone residue can easily be removed by hydrolysis.

iso*Propylidenetriazoacetohydrazide*, $N_3\cdot CH_2\cdot CO\cdot NH\cdot N\colon CMe_2$, produced by careful addition of acetone to the syrupy product from ethyl triazoacetate and hydrazine hydrate, crystallises in slender, white needles, m. p. 114°. The aqueous solution on shaking with benzaldehyde furnishes benzylidenetriazoacetohydrazide; with *p*-tolualdehyde, p-*tolylidenetriazoacetohydrazide*, $N_3\cdot CH_2\cdot CO\cdot NH\cdot N\colon CH\cdot C_6H_4Me$, is formed in white needles, m. p. 157°, whilst with benzoyl chloride in presence of sodium hydrogen carbonate, *benzoyltriazoacetohydrazide*, $N_3\cdot CH_2\cdot CO\cdot NH\cdot NHBz$, forming slender, white needles from alcohol, m. p. 145°, is produced.

a-Phenylethylidenetriazoacetohydrazide, $N_3\cdot CH_2\cdot CO\cdot NH\cdot N\colon CMePh$, can be obtained by direct condensation with the syrupy triazoacetohydrazide, forming slender, white needles from alcohol, m. p. 162°. Triazoacetohydrazide hydrochloride, previously obtained from benzylidenetriazoacetohydrazide, is more readily prepared by the hydrolysis of the *iso*propylidene-hydrazide, whilst triazoacetic acid, usually made by hydrolysing its ethyl ester, has also been derived from benzylidenetriazoacetohydrazide. Triazoacetylazoimide (Abstr., 1908, i, 145) is converted by heat into the carbimide, which with alcohol produces *triazomethylurethane*, $N_3\cdot CH_2\cdot NH\cdot CO_2Et$, a mobile, yellow oil, which decomposes without explosion on heating; it has a faint odour, and is feebly acid. With ammonia, followed by silver nitrate, silver azoimide is immediately precipitated. J. C. W.

The Hydrazide and Azoimide of α- and β-Triazopropionic Acids. THEODOR CURTIUS and HANS FRANZEN (*Ber.*, 1912, 45, 1037—1041).—The ethyl esters of α- and β-triazopropionic acids (Forster and Fierz, Trans., 1908, 93, 669) react with hydrazine hydrate, the former with considerable development of heat, the latter only on warming, to give syrupy hydrazides which can also be isolated in the form of acetone condensation products (compare preceding abstract). *iso-Propylidene-α-triazopropionohydrazide*, $N_3\cdot CHMe\cdot CO\cdot NH\cdot N\colon CMe_2$, forms colourless, shining flakes, m. p. 70°; the *benzylidene* derivative, $N_3\cdot CHMe\cdot CO\cdot NH\cdot N\colon CHPh$, crystallises in colourless, silky needles from hot alcohol, m. p. 92°. α-Triazopropionohydrazide *hydrochloride*, $N_3\cdot CHMe\cdot CO\cdot NH\cdot NH_2,HCl$, is deposited on passing dry hydrogen chloride through the ethereal solution of the *iso*propylidene-hydrazide; it forms shining needles, m. p. 107° (decomp.). On treating the *iso*propylidene-hydrazide in the required quantity of *N*-hydrochloric acid with sodium nitrite, the very explosive *α-triazopropionylazoimide*, $N_3\cdot CHMe\cdot CO\cdot N_3$, is obtained as a yellow, mobile oil with a penetrating odour. The ethereal solution when evaporated with alcohol produces *α-triazoethylurethane*, $N_3\cdot CHMe\cdot NH\cdot CO_2Et$, with evolution of nitrogen; this is a dark, mobile oil, boiling with considerable decomposition at about 100°/15 mm., and changing spontaneously into ethylidene-

diurethane (see later abstract). *β-Triazopropionohydrazide*,

$$N_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH \cdot NH_2,$$

is a clear, colourless, viscid syrup, which also can be characterised in the form of its iso*propylidene* derivative, $C_6H_{11}ON_5$, which crystallises in colourless, shining leaflets, m. p. 73°. The *benzylidene-hydrazide*, $C_{10}H_{11}ON_5$, forms colourless, silky needles from hot alcohol, m. p. 117°; the *hydrochloride*, $N_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH \cdot NH_2, HCl$, is a very hygroscopic, crystalline mass, whilst the *azoimide*, $N_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot N_3$, is a mobile, yellow, very explosive oil, yielding *β-triazopropionoanilide*, m. p. 189°, with aniline. *β-Triazoethylurethane*, $N_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO_2Et$, a faint yellow, mobile oil with pleasant odour, decomposes entirely, but without explosion when heated; it is feebly acid in warm water, and does not change with lapse of time. J. C. W.

The Hydrazide and Azoimide of γ-Triazobutyric Acid. THEODOR CURTIUS and WILHELM GIULINI (*Ber.*, 1912, 45, 1045—1050).—Quite analogous to the foregoing substances are those derived from the new γ-triazobutyric acid. *Ethyl γ-triazobutyrate*,

$$N_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2Et,$$

prepared from ethyl γ-chlorobutyrate (Henry, Abstr., 1886, 216), is a colourless, mobile liquid, b. p. 102—104°/22 mm., miscible with organic solvents, but very slightly soluble in water; in all, 1050 grams of this substance were prepared. The contribution of the triazo-group to the molecular refraction, namely, M_D 8·85, is normal, and agrees with similar values obtained by Philip (Trans., 1908, 93, 918). The ester is easily hydrolysed by 20% sodium hydroxide to the *acid*, $C_4H_7O_2N_3$, a clear, colourless liquid solidifying below 0°, b. p. 135°/11 mm.; the *sodium*, *potassium*, and *silver* salts are white. iso*Propylidene-γ-triazobutyrohydrazide*, $N_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH \cdot N{:}CMe_2$, is a white, crystalline mass, m. p. 32·5°. The *benzylidene* derivative, $C_{11}H_{13}ON_5$, crystallises in small, shining leaflets, m. p. 47°. The o-*hydroxybenzylidene* derivative forms slender needles from dilute alcohol, m. p. 105·5°, the *hydrochloride* being a yellow, gelatinous mass. *γ-Triazobutyrylazoimide*,

$$N_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot N_3,$$

prepared from the hydrazide, is a faint yellow oil, exploding when heated; with alcohol it yields *γ-triazopropylurethane*,

$$N_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO_2Et,$$

as a mobile oil which cannot be distilled, but which does not change when kept. J. C. W.

The Hydrazide and Azoimide of Triazosuccinic Acid. THEODOR CURTIUS and FRIEDRICH HARTMANN (*Ber.*, 1912, 45, 1050—1056).—The corresponding derivatives of succinic acid are in most respects similar to the substances described in the preceding abstracts. *Diethyl triazosuccinate*, $CO_2Et \cdot CH_2 \cdot CH(N_3) \cdot CO_2Et$, is obtained from the bromosuccinate and sodium azoimide under the influence of a little spongy palladium, considerable quantities of indefinite by-products being produced. It is a limpid liquid which solidifies at a very low temperature, and boils at 90—92°/0·01 mm. It is very sensitive towards alkalis, giving fumaric and hydrazoic acids (compare following abstract). *Triazosuccinohydrazide*,

$$NH_2 \cdot NH \cdot CO \cdot CH_2 \cdot CH(N_3) \cdot CO \cdot NH \cdot NH_2,$$

partly crystallises from the reaction mixture in colourless needles, m. p. 122°, readily soluble in cold water, dissolving less readily in alcohol. Hydrazine is eliminated on keeping the substance, and also on warming it with water; hence it is best converted into the *isopropylidene* compound, $C_{10}H_{17}O_2N_7$, a colourless, crystalline powder, m. p. 182·5°, soluble in hot water with decomposition. The *methylene* compound is a colourless powder almost insoluble in water, m. p. 173°; the *benzylidene* derivative, $C_{18}H_{17}O_2N_7$, is a white powder, m. p. 169°; the *o-hydroxybenzylidene* compound, $C_{18}H_{17}O_4N_7$, forms yellow flakes, m. p. 204°, whilst the *hydrochloride*, $C_4H_9O_2N_7.2HCl$, is a colourless, very hygroscopic, crystalline powder, m. p. 123°. The *iso*propylidene-hydrazide yields with nitrous acid, *triazosuccinyl azoimide*, $N_3{\cdot}CO{\cdot}CH_2{\cdot}CH(N_3){\cdot}CO{\cdot}N_3$, a yellow oil with penetrating odour; it is very unstable, exploding violently when touched or when the solution is evaporated. In the dry ethereal solution, aniline produces *triazosuccinoanilide*, $C_{16}H_{15}O_2N_5$, in colourless needles, m. p. 175°; the *p-toluidide*, $C_{18}H_{19}O_2N_5$, forms colourless needles, m. p. 201°, whilst *triazoethylenediurethane*, $CO_2Et{\cdot}NH{\cdot}CH_2{\cdot}CH(N_3){\cdot}NH{\cdot}CO_2Et$, is a dark yellow oil, soluble in warm water, decomposing when kept.

J. C. W.

Hydrolytic Degradation of Triazo-acids, Triazo-acid-azoimides, and Triazourethanes (Formation of Triazo-alkylamines). THEODOR CURTIUS (*Ber.*, 1912, 45, 1057—1093).—When hydrolysing agents are allowed to act on organic triazo-compounds, the azoimide nucleus is either eliminated as hydrazoic acid or in the form of nitrogen. Acid azoimides, which are analogous to acid chlorides, are very susceptible to the former change when attacked by sufficiently dissociated acids or alkalis. With water or alcohol, however, they lose nitrogen and undergo rearrangement to carbimides or urethanes. Aliphatic triazo-compounds, like aromatic azoimides, frequently resist simple hydrolysis, presenting marked contrast to the haloid analogues. With more powerful agents (strong acids or bases), they lose nitrogen and many of the possible changes which may occur have been observed. Such changes are illustrated as follows:

$$\text{I. } C_6H_5{\cdot}CH_2{\cdot}N_3 \xrightarrow[-N_2]{} C_6H_5{\cdot}CH{:}NH \xrightarrow{+H_2O} C_6H_5{\cdot}CHO + NH_3.$$

$$\text{II. } C_6H_5{\cdot}CH_2{\cdot}N_3 \xrightarrow{+H_2O} C_6H_5{\cdot}CH_2{\cdot}NH_2 + N_2 + [O].$$

$$\text{III. } C_6H_5{\cdot}CH_2{\cdot}N_3 \xrightarrow[-N_2]{} C_6H_5{\cdot}N{:}CH_2 \xrightarrow{+H_2O} C_6H_5{\cdot}NH_2 + CH_2O \xrightarrow{+O} H{\cdot}CO_2H.$$

They consist in, therefore, (I) partial and transitory rearrangement of the residue; (II) addition of hydrogen, producing primary amines; and (III) complete rearrangement analogous to the acid-azoimides, followed by hydrolysis and oxidation.

Benzylazoimide itself has already been shown to give on hydrolysis benzaldehyde and ammonia (I) [Abstr., 1901, 574], also methylene-aniline (III) [Curtius, 1911]. Darapsky now proves the formation of formic acid (III) (private communication). β-Triazoethylamine,

$$N_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2,$$

which is very stable towards strong alkalis, behaves in a similar manner

with concentrated hydrochloric acid, giving principally ethylenediamine (II) along with ammonia and glycine, traces of unoxidised glycinealdehyde being also recognisable (I). Scheme (III) would furnish a methylenediaminomethane, $CH_2:N\cdot CH_2\cdot NH_2$, which would at once break down into ammonia and formaldehyde, the latter being oxidised to formic acid; the presence of carbon monoxide in the liberated gases would result from the decomposition of the latter. In neither of these two cases could nitrous oxide or free oxygen be found in the liberated gases, thus contradicting the view previously held by Curtius and Darapsky (Abstr., 1901, 574).

The various fatty triazo-acids are hydrolysed by strong acids or bases more especially according to scheme (I). Thus triazoacetic acid yields ammonia and glyoxylic acid (Abstr., 1908, i, 144); α-triazopropionic acid, $CH_3\cdot CH(N_3)\cdot CO_2H$ (b. p. 121·5°/20 mm.), when heated with strong hydrochloric acid furnishes pyruvic acid, whilst traces of an α-amino-acid can be detected. *β-Triazopropionic acid*, $N_3\cdot CH_2\cdot CH_2\cdot CO_2H$, a yellow oil with rancid odour, could not be obtained from its ester by means of alkali, as this eliminates hydrazoic acid and leaves acrylic acid (Forster and Fierz, Trans., 1908, 93, 669); nevertheless, the ester, the hydrazide, or its acetone derivative may be smoothly hydrolysed by dilute acids. Strong hydrochloric acid degrades the ester to acetaldehyde and carbon dioxide, traces of glycine being also detected (III). γ-Triazobutyric acid, in the form of its ethyl salt, is hydrolysed by concentrated hydrochloric acid to ammonia, ethyl aldehydopropionate, $CHO\cdot CH_2\cdot CH_2\cdot CO_2Et$, and β-aldehydopropionic acid itself. This semialdehyde of succinic acid is easily converted into succinic acid (Perkin and Sprankling, Trans, 1899, 75, 11); the hydrolysis thus provides an interesting conversion of butyric into succinic acid. Probably γ-aminobutyric acid and β-alanine (II and III) are also produced. Ethyl triazosuccinate, when hydrolysed by means of sulphuric acid, furnishes ammonia, pyruvic acid, and carbon dioxide, the latter substances being the decomposition products of the expected ethyl aceto-oxalate (I). Towards alkalis, however, it is very sensitive, decomposing into fumaric and hydrazoic acids. With strong ammonia, fumaramide, ammonium azoimide and apparently ethyl iminosuccinamate, $CO_2Et\cdot CH_2\cdot C(:NH)\cdot CO\cdot NH_2$, are produced; the latter crystallises from alcohol in colourless tablets, m. p. 120°, is very sweet to the taste, and decolorises alkaline permanganate. Dilute alkalis liberate two molecules of ammonia, whilst sulphuric acid yields pyruvic acid and carbon dioxide, which arise from the intermediate ethyl oxalacetate. It is probably identical with Thomas-Mamert's "stereoisomeride" of ethyl aminofumaramate, (Abstr., 1895, i, 267).

Hydrolysis of those triazourethanes in which the triazo-group adjoins the urethane-nitrogen, yields hydrazoic acid and other degradation products. Thus, triazomethylurethane, even on boiling with water, gives (possibly) *hydroxymethylurethane*, $HO\cdot CH_2\cdot NH\cdot CO_2Et$, as slender, white needles, m. p. 64°, which decompose with sulphuric acid into formaldehyde and carbon dioxide. It was not found possible to obtain such a substance directly from glycolylazoimide, $HO\cdot CH_2\cdot CO\cdot N_3$. α-Triazoethylurethane undergoes a similar change with boiling water or dilute acids, giving acetaldehyde, etc.; it also suffers gradual

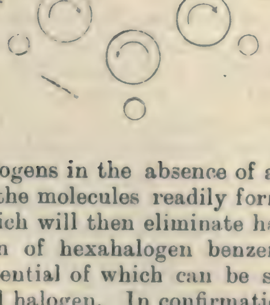
hydrolysis, the ethylidenediurethane of Nencki (*Ber.*, 1874, **7**, 160), crystallising out from the oil with liberation of hydrazoic acid. Moist triazoethylenediurethane also decomposes after a time, yielding a substance, m. p. 60—65°, which is probably *ethanetriurethane*,

$$CO_2Et\cdot NH\cdot CH_2\cdot CH\cdot (NH\cdot CO_2Et)_2.$$

On the other hand, those urethanes in which the triazo-group is removed from the urethane-nitrogen furnish triazoalkylamines, which are remarkably stable towards strong alkalis, losing nitrogen when hydrolysed by acids and giving rise to diamines (scheme II.). Thus, β-triazoethylurethane yields with baryta the β-triazoethylamine of Forster and Newman (Trans., 1911, **99**, 1279), whilst γ-triazopropylurethane gives the γ-triazopropylamine recently described by Forster and Withers (Trans., 1912, **101**, 490). The *picrate* forms golden-yellow prisms from alcohol, m. p. 96°, and the contribution of the triazo group to the molecular refraction (M_D 8·82) is normal. Hydrolysis with strong hydrochloric acid yields trimethylenediamine, whilst the liberated gas contains 1 mol. nitrogen, a small amount of carbon monoxide, but no oxygen or nitrous oxide. J. C. W.

Stereochemistry of the Aromatic Series. EDMUNDO LOZANO (*Anal. Fis. Quim.*, 1912, **10**, 81—82).—Polemical against the originality and validity of the formula proposed by Casares (compare Abstr., i, 247). G. D. L.

The Configuration of Benzene, the Mechanism of Benzene Substitution, and the Contrast between the Formation of Para-, Ortho-, and of Meta-substitution Products. JACOB BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **14**, 1066—1081).—The author has already pointed out that for the retention of two homonymous atoms within a molecule, a certain inequality or contrast must be assumed which may possibly be caused by an adverse movement of the corpusculæ. By combining this idea with Werner's fundamental principle of the universal affinity he arrives at the annexed formula for benzene. This shows not only the contrast between the ortho-, para-, and meta-, but also the equality of the two ortho-placed carbon atoms.



The extreme slowness with which benzene undergoes substitution by halogens in the absence of a catalyst is attributed to the small chance of the molecules readily forming additive products of higher potential which will then eliminate halogen acid. Only the case of the formation of hexahalogen benzene compounds results in a condition the potential of which can be smaller than that of a mixture of benzene and halogen. In confirmation of this, van der Linden has noticed that when an insufficiency of halogen is added to benzene, hexahalogen benzene is obtained, which does not contain appreciable quantities of

lower additive products. The rôle of the catalyst in the formation of halogen substitution products of benzene is supposed to depend on its ability to promote the entrance of halogen into the benzene in such a manner that the simplest additive product is first formed.

Generally, a catalyst can cause a modification in the condition of benzene as well as in that of the acting molecule. Should the latter alone be affected, hexahalogen additive products result (action of benzene and halogen under influence of light or hypohalogenic acid). If, however, the benzene molecule is entered by the catalyst, then the second molecule, which may also have been made active, will be able to act there, and the formation of mono-substitution products is to be expected (action of $FeCl_3$,$AlCl_3$). In the cases of nitration and sulphonation of benzene, which occur readily, the velocity is largely dependent on the concentration of the acid, so that it increases at a much greater rate than corresponds with the strength of the acid. Here it is assumed that nitrogen pentoxide and sulphur trioxide act at catalysts.

In considering the further substitution of mono-substituted derivatives of benzene, the author points out that two influences are operative, namely, the disturbance of equilibrium in the benzene molecule occasioned by the substituent already present, and the affinity of the group present towards the entering molecule. He distinguished three general cases: (1) The affinity of the entering molecule (B) for the substituent present (X) is very great. B will then act in the first place on X, and be retained therein, after which action ceases (reduction of the nitro-group, oxidation of the –SH-group, etc.). (2) The affinity of the acting molecule B for X is less considerable, so that, at most, labile additive products can be retained. The group B will then further accentuate the disturbance of the equilibrium caused by X, and the molecule enter into the nucleus in the ortho-para-position (chlorination of sulphides, amides, bromides, iodides; hydrogenation of phthalic and terephthalic acids, etc.). (3) The affinity of the acting molecule B for X is not present. X will then oppose the addition and substitution in the ortho-para-position, so that the influence of the disturbance of the equilibrium can be lessened or destroyed by this adverse action, thus the *m*-substitution can become predominant (nitration, sulphonation, and chlorination of nitro-compounds, sulphonic and carboxylic acids, hydrogenation of amino- and hydroxy-compounds). H. W.

New Method for the Preparation of Hydrocarbons of the Styrene Group. I. Allylbenzene and its Homologues. FRANZ KUNCKELL [and WILHELM DETTMAR] (*Ber. Deut. Pharm. Ges.*, 1912, **22**, 180—199).—The paper consists of a re-statement of earlier results (Kunckell and Dettmar, Abstr., 1903, i, 331; Kunckell, Abstr., 1903, i, 617), together with some further details as to derivatives of the products.

Propenylbenzene gives *αβ-dibro opropylbenzene*, CHPhBr·CHMeBr, colourless needles, m. p. 66—67°. The action of alcoholic potash on α-chloro-β-bromopropenylbenzene apparently removes the elements of hydrogen chloride, giving a *substance* of unknown constitution, b. p. 232—238°, 122—130°/19 mm.

1-*Methyl*-4-*αβ-dibromopropylbenzene* is a colourless, oily liquid, b. p. 140—143°/10 mm., D^{18} 1·609; the *nitrosochloride* is a colourless solid, m. p. 135°.

1-*Ethyl*-4-*αβ-dibromopropylbenzene* has b. p. 162—165°/16 mm., D^{18} 1·574.

1-iso*Propyl*-4-*αβ-dibromopropylbenzene* has b. p. 169—172°/20 mm., D^{18} 1·512.

1-*Methyl*-4-iso*propyl*-3-*αβ-dibromopropylbenzene* has b. p. 167—170°/19 mm., D^{18} 1·432.

1 : 2-*Dimethyl*-4-*αβ-dibromopropylbenzene* has b. p. 165—168°/16 mm., D^{18} 1·591. D. F. T.

New Method for the Preparation of Hydrocarbons of the Styrene Group. II. α-Phenyl-Δ^{α}-butylene and Its Homologues. FRANZ KUNCKELL (*Ber. Deut. Pharm. Ges.*, 1912, 22, 242—251).—A recapitulation and extension of the results obtained in the preparation of derivatives of α-phenyl-Δ^{α}-butylene from phenyl propyl ketone derivatives (compare Kunckell and Siecke, Abstr., 1903, i, 331; Kunckell, Abstr., 1903, i, 617).

α-p-*Tolyl*-Δ^{α}-*butylene dibromide* [*αβ-dibromobutyltoluene*],

$$C_6H_4Me\cdot CHBr\cdot CHBr\cdot CH_2Me,$$

is a pale yellow oil, b. p. 164—167°/18 mm.; the corresponding *dichloride* is a pale yellow liquid, b. p. 261—266°, or 124—129°/6 mm.; *additive compound*, with hydrogen chloride, a reddish-yellow oil; *nitrosochloride*, crystalline scales, m. p. 148° (decomp.).

o-, *m*-, and *p*-Xylene each give a set of derivatives. Three *xylyl-α-bromopropyl ketones*, $C_6H_3Me_2\cdot CO\cdot CHBr\cdot CH_2Me$, were obtained: 1 : 2 : 4, a liquid of irritating odour, b. p. 157—160°/8 mm.; 1 : 3 : 4, b. p. 167—172°/17 mm.; 1 : 4 : 3, b. p. 159—161°/16 mm. Three *α-chloro-β-bromo-α-xylyl-Δ^{α}-butylenes*, $C_6H_3Me_2\cdot CCl\!:\!CBr\cdot CH_2Me$: 1 : 2 : 4, colourless liquid of strong aromatic odour, b. p. 154—160°/17 mm.; 1 : 3 : 4, b. p. 144—154°/20 mm.; 1 : 4 : 3, b. p. 150—155°/16 mm. These by reduction yield three *α-xylyl-Δ^{α}-butylenes*,

$$C_6H_3Me_2\cdot CH\!:\!CH\cdot CH_2Me:$$

1 : 2 : 4, an oil with aniseed odour, b. p. 238—239°, 122—124°/18 mm., D^{15} 0·9114, n^{20} 1·5458, *dibromide*, pale yellow oil, b. p. 155—157°/6 mm.; 1 : 3 : 4, colourless, aromatic liquid, b. p. 226—228°, or 109—111°/16 mm., D^{18} 0·8967, n^{20} 1·5349, *dibromide*, pale yellow liquid, b. p. 167—169°/15 mm.; 1 : 4 : 3, liquid of aromatic odour, b. p. 221°, or 117—120°/17 mm., D^{18} 0·8958, n^{20} 1·5280, *dibromide*, colourless leaflets, m. p. 75°, b. p. 166—168°/16 mm.

Ethylbenzene gives p-*ethylphenyl α-bromopropyl ketone*, a very pale yellow liquid, b. p. 152—154°/7 mm.; *α-chloro-β-bromo-α*-p-*ethylphenyl-Δ^{α}-butylene*, b. p. 140—145°/6 mm., and *α*-p-*ethylphenyl-Δ^{α}-butylene*, a colourless liquid of aniseed odour, b. p. 230—233°, or 98—102°/7 mm., D^{20} 0·9074, n^{20} 1·5405; the *dibromide* of the last substance is almost colourless, b. p. 146—149°/6 mm.

Cumene gives *α*-p-iso*propylphenyl α-bromopropyl ketone*, b. p. 153—160°/8 mm.; *α-chloro-β-bromo-α*-p-iso*propylphenyl-Δ^{α}-butylene*, a pale yellow oil, b. p. 145—155°/8 mm., and *α*-p-iso*propylphenyl-Δ^{α}-butylene*, a yellow oil, b. p. 242—243°, or 131—139°/17 mm., D^{14} 0·8932, n^{20} 1·5330; the last-named gives a *dibromide*, b. p. 152—157°/10 mm.

Cymene gives 3-*methyl*-6-iso*propylphenyl* α-*bromopropyl ketone*, b. p. 152—155°/8 mm.; α-*chloro*-β-*bromo*-α-3-*methyl*-6-iso*propylphenyl*-Δ^{α}-*butylene*, b. p. 152—159°/16 mm., and α-3-*methyl*-6-iso*propylphenyl*-Δ^{α}-*butylene*, a pale yellow liquid, b. p. 241—244°, D^{14} 0·9353, n^{20} 1·5274; the *dibromide* of the last has b. p. 150—152°/7 mm. D. F. T.

New Applications of the Grignard Reaction. JULIUS VON BRAUN, H. DEUTSCH, and A. SCHMATLOCH (*Ber.*, 1912, **45**, 1246—1263).—It has already been observed that the conversion of phenoxylated iodides of the type $C_6H_5\cdot O\cdot(CH_2)_x\cdot I$ into phenoxyolefines by way of the quaternary ammonium iodides and the ammonium hydroxides does not proceed smoothly when the chain X has more than six members (compare Abstr., 1907, i, 28). It is now found that when the iodine is sufficiently removed from the phenol nucleus, the iodides give true Grignard compounds, which furnish the desired olefines when treated with allyl bromide, a reaction similar to that discovered by Tiffeneau, namely, that magnesium phenyl bromide and allyl bromide readily yield allylbenzene.

Two of the lowest members of the series, bromophenetole (Grignard, Abstr, 1904, i, 494) and γ-phenoxypropyl iodide, do not react in the normal way with magnesium, but already with δ-phenoxybutyl iodide 70% of the substance does react, yielding with water *n*-phenoxybutane, 1 : 8-diphenoxyoctane also being formed by the synthetic action of the metal. Similarly, ε-phenoxyamyl iodide furnishes *phenoxypentane*, $C_6H_5\cdot O\cdot[CH_2]_4\cdot CH_3$, a pleasant smelling oil, b. p. 111°/17 mm., volatile in steam, and non-volatile *ακ-diphenoxydecane*, $OPh\cdot[CH_2]_{10}\cdot OPh$, m. p. 86°, whilst the action of oxygen on the magnesium compound produces *ε-phenoxyamyl alcohol*, $OPh\cdot[CH_2]_5\cdot OH$, as a glycerol-like liquid, b. p. 150—155°/11 mm., which gives an oily benzoyl derivative and a well-defined *phenylurethane*, $OPh\cdot[CH_2]_5\cdot O\cdot CO\cdot NHPh$, m. p. 93°. The same magnesium compound reacts with trioxymethylene to give *ζ-phenoxyhexyl alcohol*, a similar syrupy liquid, b. p. 175°/13 mm., the *phenylurethane*, $C_{19}H_{23}ON_3$, of which melts at 102°, but with ethylene chlorohydrin, however, it only yielded traces of phenoxyheptyl alcohol. Attempts to convert these Grignard compounds into acetals and thus into aldehydes by means of ethyl orthoformate have not succeeded, but the nitro-method which led to aliphatic dialdehydes and fatty-aromatic aldehydes (compare Abstr., 1911, i, 830; 1912, i, 265) may prove useful in the case of these iodides. From γ-phenoxypropyl iodide and silver nitrite, *γ-nitro-α-phenoxypropane* $OPh\cdot[CH_2]_3\cdot NO_2$, is obtained as a pale yellow, pleasant smelling liquid, b. p. 171—177°/17 mm., which on reduction yields *phenoxypropionaldoxime*, $OPh\cdot[CH_2]_2\cdot CH\!:\!NOH$, m. p. 142°; *ε-nitro-α-phenoxypentane*, $OPh\cdot[CH_2]_5\cdot NO_2$, b. p. 203—209°/16 mm., and *phenoxyvaleraldoxime*, $OPh\cdot[CH_2]_4\cdot CH\!:\!NOH$, m. p. 112—113°, are prepared in the same way.

Tiffeneau's application of allyl bromide, which has also been made use of by de Reséguier in the preparation of allyl*cyclo*hexane (Abstr., 1910, i, 467), has now been extended to a variety of magnesium-halogen compounds, and is shown to be very valuable in the building up of aromatic compounds with long side-chains. Besides the allyl products, $X\cdot C_3H_5$, which are often produced in 70% yields, condensed hydrocarbons, X·X, are also formed. Octyl bromide gives

undecylene and hexadecane; $\alpha\epsilon$-di-iodopentane gives undecadiene, recently described by Reformatzky (Abstr., 1911, i, 597), oxidation to azelaic acid confirming the position of the unsaturated linking; $\alpha\delta$-di-iodobutane yields $\Delta^{\alpha\iota}$-*decadiene*, $CH_2\!:\!CH\cdot[CH_2]_6\cdot CH\!:\!CH_2$, a sweet smelling liquid, b. p. 170°, which appears to be identical with the hydrocarbon from decamethylenebistrimethylammonium hydroxide (this vol., i, 165). In the same way phenylethyl bromide gives phenylamylene (Abstr., 1911, i, 613), the position of the ethenoid linking being shown by the fact that only after prolonged heating with saturated hydrobromic acid does addition take place, the resulting *δ-bromo-α-phenylpentane*, $C_6H_5\cdot[CH_2]_3\cdot CHMe\cdot Br$, b. p. 137—139°/13 mm., differing from the isomeric ε-phenylamyl bromide (this vol., i, 106) in that it has a much less intense odour. The bromine atom is only exchanged for cyanogen after heating with potassium cyanide for many days; the *nitrile*, $CH_2Ph\cdot[CH_2]_2\cdot CHMe\cdot CN$, is a colourless, faintly smelling liquid, b. p. 150—154°/in vacuum, which hydrolyses with difficulty to *δ-phenyl-α-methylvaleric acid*, $C_6H_5\cdot[CH_2]_3\cdot CHMe\cdot CO_2H$, b. p. 178°/8 mm., giving a white silver salt, but not crystallising (compare Abstr., 1911, i, 969: ε-phenylhexoic acid). From phenylpropyl bromide, magnesium and allyl bromide, the very pleasant smelling *phenylhexylene*, $CH_2Ph\cdot[CH_2]_3\cdot CH\!:\!CH_2$, is obtained, b. p. 94—95°/10 mm., D_4^{20} 0·8839, n_D^{20} 1·5033. With similar difficulty it unites with hydrogen bromide, the *ε-bromo-α-phenylhexane*,

$$CH_2Ph\cdot[CH_2]_3\cdot CHMeBr,$$

boiling at 152—156°/10 mm., and yielding a magnesium compound which decomposes with trioxymethylene, giving *ζ-phenyl-β-methylhexyl alcohol*, $CH_2Ph\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot OH$, b. p. 160—163°/13 mm., which has a sweet odour, more intense than that of phenylheptyl alcohol and more pleasant than that of ζ-phenylhexyl alcohol. Phenylamyl bromide, $CH_2Ph\cdot[CH_2]_3\cdot CH_2Br$, b. p. 144°/12 mm., from ε-phenylamyl alcohol and hydrobromic acid, gives a somewhat poorer yield of *phenyloctylene*, $CH_2Ph\cdot[CH_2]_5\cdot CH\!:\!CH_2$, a pleasant smelling, colourless liquid, b. p. 115—117°/8 mm., D_4^{20} 0·8792, n_D^{20} 1·4995. From δ-phenoxybutyl iodide, besides some diphenoxyoctane, phenoxyheptene, $OPh\cdot[CH_2]_5\cdot CH\!:\!CH_2$, is obtained; this readily absorbs bromine, the somewhat unstable dibromide being hydrolysed with difficulty by means of fuming hydrobromic acid, yielding *αβη-tribromoheptane*, $CH_2Br\cdot[CH_2]_4\cdot CHBr\cdot CH_2Br$, a colourless liquid having a pleasant, spicy odour and boiling at 150—155°/8 mm. Similarly, phenoxyoctene, $CH_2Ph\cdot[CH_2]_5\cdot CH\!:\!CH_2$, from ε-phenoxyamyl iodide, may be converted into *αβθ-tribromo-octane*, $CH_2Br\cdot[CH_2]_5\cdot CHBr\cdot CH_2Br$, b. p. 160°/10 mm.

These tribromo-paraffins, like αβε-tribromohexane (Abstr., 1911, i, 938), react with magnesium, losing the neighbouring bromine atoms and yielding unsaturated magnesium compounds, but the conversion of these into unsaturated iodides by means of iodine is unsatisfactory, the ethenoid linking absorbing the halogen to a great extent. It is now found, however, that iodoacetonitrile brings about the desired change and that it reacts generally like the free element, converting, for example, bromobenzene into iodobenzene and phenylpropyl bromide into phenylpropyl iodide, b. p. 118—123°/10 mm., which is characterised by conversion into phenylbutyronitrile (Abstr., 1910, i, 843), and into

phenylbutyric acid itself. In the case of $\alpha\beta\epsilon$-tribromohexane, a certain mount of an unsaturated hydrocarbon, probably

$$CHMe:CH\cdot[CH_2]_6\cdot CH:CHMe,$$

is obtained, but the presence of iodohexylene, $CHMe:CH\cdot[CH_2]_2\cdot CH_2I$, is shown by its conversion in the crude state into a nitrile and then into Δ^δ-heptenoic acid, $CH_3\cdot CH:CH\cdot[CH_2]_3\cdot CO_2H$. The formation of iodoheptylene from $\alpha\beta\eta$-tribromoheptane is also proved by treating the crude product with trimethylamine, when, besides a small amount of *trimethylcyanomethylammonium iodide*, $NMe_3I\cdot CH_2\cdot CN$, m. p. 196°, from unchanged iodoacetonitrile, the recently described trimethyl-Δ^ζ-heptenylammonium iodide (Abstr., 1912, i, 165) is obtained; this confirms the position of the three bromine atoms, and hence of the ethylene linking in phenoxyheptene. For synthetic purposes it appears unnecessary to isolate the unsaturated iodide from the crude product.

J. C. W.

The Action of Aluminium Chloride on the Homologues of Benzyl Chloride. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1912, 45, 1267—1274).—Inspired by Kipping's discovery that fatty-aromatic acid chlorides produce cyclic ketones under the influence of aluminium chloride (see Trans., 1894, 65, 480; 1899, 75, 144; 1901, 79, 602), the authors have tried the action of this reagent on their oxygen-free fatty-aromatic chlorides, with the hope of finding the conditions for ring formation. They have found that the substitution of $-CH_2$ for $-CO$ in the side-chain is of enormous influence, considerably diminishing the tendency to the formation of benzene derivatives of five- or seven-membered rings.

Phenylbutyl chloride was converted by this means into pure tetrahydronaphthalene previously obtained from naphthalene in a less pure form by Bamberger and Kitschelt (Abstr., 1890, 1146); contrary to this earlier notice, it was found to have an odour like hydrindene, did not change in the air, nor decolorise bromine, and was only slowly attacked by permanganate; b. p. 205°, D_4^{20} 0·957, n_D^{20} 1·5370. Phenylpropyl chloride, however, gave only a trace of hydrindene, although phenylpropionyl chloride is converted to the extent of 95% into α-hydrindone (Thiele and Wanscheidt, Abstr., 1910, i, 831); the chief product, which is not volatile in steam, is a viscid, chlorine-free, red oil, probably a combination of several molecules of the chloride with elimination of hydrogen chloride. A mixture of such compounds is the only result in the case of phenylethyl chloride. Phenylamyl chloride in light petroleum or carbon disulphide solution is converted into a similar mixture (35%), but chiefly into a peppermint-like oil which distilled in steam (60%); potassium permanganate removed a small amount of unsaturated hydrocarbons from this, leaving phenyl*cyclo*pentane (compare Borsche and Menz, Abstr., 1908, i, 149). In benzene solution, however, the portion not volatile in steam was not a complicated mixture, but *$\alpha\epsilon$-diphenylpentane*, $CH_2(CH_2\cdot CH_2Ph)_2$, a glycerol-like liquid, b. p. 190—200°/12 mm. The formation of phenyl*cyclo*pentane, the constitution of which is confirmed by oxidation to benzoic acid and not to phthalic acid, as the latter would agree with benzosuberane, is a case in which aliphatic hydrogen is removed in an

elimination of hydrogen chloride, and instances a new course of the Friedel and Craft's reaction. That the *cyclo*pentane ring does not hinder substitution in the benzene ring is shown by the formation of p-(?)-*nitrophenyl*cyclo*pentane*, $NO_2\cdot C_6H_4\cdot C_5H_9$, a yellow oil with pleasant odour, b. p. 162—169°/13 mm. J. C. W.

Electrolytic Reduction of Nitrobenzene without a Diaphragm. E. F. FARNAU (*J. Physical Chem.*, 1912, **16**, 249—252. Compare Snowdon, this vol., i, 100).—Snowdon's method of electrolysing an emulsion of nitrobenzene between iron electrodes when carried out at ordinary temperatures (25°, rising to 35°) with sodium sulphate solution as electrolyte instead of ferrous chloride gives a good yield of aniline.

Both cathodic hydrogen and ferrous sulphate act as reducing agents. In the author's experiments the reduction was not carried to completion, and the average current efficiency calculated on the aniline produced was 78%. It is stated that no reduction product other than aniline was obtained, but about 12% of the nitrobenzene was unaccounted for. R. J. C.

Nitration of *o*-Tolyl *p*-Toluenesulphonate. FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1912, [iv], **11**, 447; *Ber.*, 1912, **45**, 1450).—In a previous paper with P. Crépieux (Abstr., 1902, i, 435), the author described *o*-tolyl *p*-toluenesulphonate as yielding on nitration 3:5-dinitro-*o*-tolyl *p*-toluenesulphonate, m. p. 108—109°. He now finds that the substance so described was really 5-*nitro*-o-*tolyl* 2-*nitro*-p-*toluenesulphonate* (compare Ullmann and Sané, this vol., i, 104). T. A. H.

Unsaturated Compounds. I. Elimination of Hydrogen Chloride from Unsymmetrical Carbinyl Chlorides. ALEX. ORECHOFF and R. KONOWALOFF (*Ber.*, 1912, **45**, 861—865).—On elimination of hydrogen chloride from dibenzylphenylethylcarbinyl chloride, $CH_2Ph\cdot CH_2\cdot CCl(CH_2Ph)_2$, by heating with pyridine, the formation of two unsaturated hydrocarbons is possible. By oxidation of the product with ozone, benzaldehyde is obtained, proving that the hydrocarbon obtained has the constitution

$$CH_2Ph\cdot CH_2\cdot C(CH_2Ph){:}CHPh.$$

The nearest phenyl radicle in this case has the strongest displacing influence on the hydrogen of the methylene group. It is proposed to test whether this is a general rule.

Dibenzylphenylethylcarbinol, prepared by the interaction of ethyl phenylpropionate with benzyl chloride and ether, crystallises in small, colourless needles, m. p. 62—63°.

Dibenzylphenylethylcarbinyl chloride, obtained by the action of dry hydrogen chloride on the carbinol dissolved in ether, forms colourless needles, m. p. 108°.

β-Phenyl-α-benzyl-α-phenylethylethylene [*αδ-Diphenyl-β-benzyl-Δ^{α}-butylene*] crystallises in well-formed, colourless needles in stellate aggregates, m. p. 57—58°. E. F. A.

Hexahydrotriphenylmethane and its Derivatives. JULIUS SCHMIDLIN and ROBERT VON ESCHER (*Ber.*, 1912, 45, 889—899).—Hexahydrotriphenylmethane [diphenyl*cyclo*hexylmethane] is obtained by reduction of hexahydrotriphenylcarbinol or from diphenyl*cyclo*hexylidenemethane. The hydroxyl group of hexahydrotriphenylcarbinol is very mobile, but substitution is prevented by the proximity of the *cyclo*hexane ring; in such cases, water is eliminated and diphenyl*cyclo*hexylidenemethane obtained. No carbinyl chloride could be isolated after the mild action of hydrogen chloride. When hydrogen chloride is allowed to act directly on the unsaturated hydrocarbon or on the carbinol at a higher temperature, *diphenylchloro*cyclo*hexylmethane*, $CHPh_2\cdot CCl<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH_2$, isomeric with the carbinol chloride is readily obtained. The instability of the carbinol chloride points to a similar instability in the dyes derived from hexahydrotriphenylmethane.

To prepare hexahydroleucomalachite-green (Zelinsky and Gutt, Abstr., 1907, i, 709), magnesium *cyclo*hexyl bromide is caused to react with *p*-dimethylaminobenzaldehyde, and the *p*-dimethylaminophenyl*cyclo*hexylcarbinol formed (Schmidlin and Escher, Abstr., 1908, i, 163) is condensed with dimethylaniline.

Crystalline oxidation products of hexahydroleucomalachite-green could only be obtained using Caro's acid, when a dioxide,

$$(O\colon NMe_2\cdot C_6H_4)_2CH\cdot C_6H_{11},$$

is formed.

On oxidation in acetic acid solution with very little lead peroxide or ozone, a fairly marked bluish coloration is produced, which in time vanishes, particularly on the addition of mineral acids.

*Diphenyl*cyclo*hexylmethane* forms prismatic crystals, m. p. 56·5°.

*Diphenylchloro*cyclo*hexylmethane* crystallises in colourless leaflets, m. p. 120—122° (corr.).

*Diphenylbromo*cyclo*hexylmethane* separates in colourless, lustrous crystals, m. p. 125° (corr.).

The dioxide of hexahydroleucomalachite-green crystallises in lustrous, colourless plates, m. p. 165° (corr.).

p-*Methoxyphenyl*cyclo*hexylcarbinol*, $OMe\cdot C_6H_4\cdot CH(OH)\cdot C_6H_{11}$, prepared from bromo*cyclo*hexane, magnesium, and anisaldehyde, forms long, colourless needles, m. p. 92° (corr.).

p-*Methoxyphenyl*cyclo*hexylcarbinyl chloride* separates in crystals, m. p. 104° (corr.); when boiled with water, it is converted into the carbinol. E. F. A.

Autoreduction of Triphenylmethyl under the Action of Light. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÚS (*Ber.*, 1912, 45, 1344—1350).—Complete decolorisation occurs when a benzene solution of pure triphenylmethyl is exposed to diffused light, quantitative decomposition into triphenylmethane and diphenyldi-biphenylene-ethane taking place:

$$6C(C_6H_5)_3 = 4CH(C_6H_5)_3 + \begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>CPh\cdot CPh<\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}.$$

The reaction appears to depend on the reduction of hexaphenylethane to diphenyldi-biphenylene-ethane by the triphenylmethyl. Complete decolorisation is only observed when pure triphenylmethyl is employed. When heat or impure metal is used in the preparation of the latter substance, yellow impurities, stable towards light, are readily introduced.

Pure triphenylmethyl dissolved in benzene was exposed to light during forty-five days. The colourless solution had deposited crystals of diphenyldi-biphenylene-ethane, which were filtered and exposed to air in benzene solution, whereby phenyldiphenylenecarbinyl peroxide, $C_{38}H_{26}O_2,2C_6H_6$, m. p. 209° (corr.), was obtained, the identity of which was proved by comparison with phenyldiphenylenecarbinyl peroxide obtained from phenyldiphenylenecarbinol. The mother liquor yielded triphenylmethane, together with a small additional quantity of diphenyldi-biphenylene-ethane. Solutions of triphenylmethyl remained unchanged when preserved in the dark during three months.

Triphenylmethyl, when heated during forty-eight hours in xylene solution, yielded triphenylmethane, together with a large quantity of a non-crystalline, fluorescent, yellow substance. When heated in benzene solution at 100° during four months, it yielded only crystalline products, chiefly a *substance*, m. p. 165°, which is coloured red by concentrated sulphuric acid. No triphenylmethane could be detected.

H. W.

The Behaviour of Monohalogenanilines. OTTO FISCHER and PETER NEBER (*Ber.*, 1912, **45**, 1093—1098).—The behaviour of *o*-chloroaniline is in many respects peculiar. With regard to the formation of benzylidene compounds, and the action of nitrous acid on *o*-halogenmonomethylanilines or *o*-chloroacetanilide, however, these substances behave similarly to, for example, *m*-chloroaniline.

By the condensation of *o*-chloroaniline with the respective aldehydes, the following derivatives were obtained: *benzylidene*-o-*chloroaniline*, m. p. 33—34°; o-*hydroxybenzylidene*-o-*chloroaniline*, m. p. 79°; p-*hydroxybenzylidene*-o-*chloroaniline*, m. p. 162°; o-*nitrobenzylidene*-o-*chloroaniline*, m. p. 111°; p-*nitrobenzylidene*-o-*chloroaniline*, m. p. 121°; p-*methoxybenzylidene*-o-*chloroaniline*, m. p. 58°; from *o*-bromoaniline were obtained o-*hydroxybenzylidene*-o-*bromoaniline*, m. p. 84°, and p-*hydroxybenzylidene*-o-*bromoaniline*, m. p. 162°.

o-*Chloro*-N-*nitrosoacetanilide*, m. p. 47°, was prepared by passing nitrous fumes into a well-cooled solution of *o*-chloroacetanilide in glacial acetic acid.

o-Chloroaniline was treated successively with methyl sulphate and nitrous acid. The oily nitrosoamine, when acted on by concentrated hydrochloric acid, was transformed into o-*chloro*-p-*nitrosomethylaniline*, m. p. 131—132°, which gave o-*chloro*-p-*nitrosophenol*, m. p. 148° (decomp.), when heated with sodium hydroxide. *o*-Bromoaniline, when similarly treated, yielded o-*bromo*-p-*nitrosomethylaniline*, m. p. 104°. Similarly, from *m*-chloroaniline, m-*chlorophenylmethylnitrosoamine*, m. p. 37—38°, was prepared, which was transformed into m-*chloro*-p-*nitrosomethylaniline*, m. p. 134—136° (decomp.), by the action of cold hydrochloric acid.

H. W.

The Nitrosoamine Rearrangement with Hydrobromic Acid. OTTO FISCHER [with HANS GROSS] (*Ber.*, 1912, **45**, 1098—1103).—Nitrosoamines are converted into *p*-nitroso-bases by means of hydrochloric acid in alcoholic, aqueous, or glacial acetic acid solution. It is advisable to choose that solvent in which the hydrochloride of the nitroso-base is least soluble. Disturbing factors arise through the oxidation of the eliminated nitric oxide by means of air, and the reaction of the nitrogen peroxide with hydrochloric acid, resulting in the liberation of chlorine and the formation of chlorinated by-products. These disturbing influences are more marked when hydrobromic acid is substituted for hydrochloric acid.

A cold ethereal solution of phenylmethylnitrosoamine, when acted on by an alcoholic solution of hydrobromic acid, precipitated the hydrobromides of methylaniline, *p*-nitrosomethylaniline, *p*-bromomethylaniline, and *o-p*-dibromomethylaniline, the latter in very small quantity, whilst the mother liquor contained phenylmethylnitrosoamine, *p*-bromophenylmethylnitrosoamine, together with the hydrobromides of methylaniline, *p*-bromomethylaniline, and *p*-nitrosomethylaniline. Larger quantities of the above-mentioned *o-p*-dibromomethylaniline can be obtained when phenylnitrosoamine is added to a well-cooled aqueous solution of hydrobromic acid (D 1·78). o-p-*Dibromophenylmethylnitrosoamine* has m. p. 50°.

If the para-position in the nitrosoamine be already occupied, an almost quantitative transformation into the secondary base can be brought about by hydrobromic acid; thus *p*-bromophenylmethylnitrosoamine yields *p*-bromomethylaniline.

Diphenylnitrosoamine, when dissolved in a mixture of alcohol and ether and treated with alcoholic hydrobromic acid, yielded diphenylamine and di-*p*-bromodiphenylamine. H. W.

Action of Methyl Iodide and Alkali on *p*-Nitrosodimethylaniline. OTTO FISCHER and EDUARD HEPP (*Ber.*, 1912, **45**, 1103—1104).—Contrary to the statement of von Pechmann and Seel (Abstr., 1898, i, 309), the authors find that tetramethyldiaminoglyoxime *N*-phenyl ether is formed when the methiodide of *p*-nitrosodimethylaniline is treated with sodium hydroxide. H. W.

Action of Concentrated Sulphuric Acid on Some Aromatic Nitrosamines. III. FRÉDÉRIC REVERDIN and FRANZ LIEBL (*Arch. Sci. phys. nat.*, 1912, [iv], **33**, 332—338.* Compare Abstr., 1910, i, 255; 1911, i, 123).—With the object of determining whether the reduction of secondary nitroamines to nitrosoamines by sulphuric acid is general, derivatives of *o*- and *p*-phenetidine have been prepared. These readily undergo oxidation, so although the formation of nitrosoamines does indeed take place, the yields are very poor, being much less than in the former cases. The course of the reaction is not clear, although the liberation of carbon dioxide, oxygen, nitrogen, and sometimes oxides of nitrogen would suggest a complete destruction of part of the substance; slight changes in the experimental conditions modify the result to such an extent that comparative studies are well-nigh impossible. It may be that the nitro-group is set free to oxidise a part of the molecule

* and *Bull. Soc. chim.*, 1912, [iv], **11**, 485—490.

and then becomes fixed as a nitroso-group, for it is found that such resistant nitroamines as the highly oxidised trinitromethylnitroaniline scarcely react, whilst in the case of those nitroamines which are only slightly substituted, the nitro-group is free to wander in the nucleus and the formation of nitrosoamines is likewise avoided.

Dimethyl-o-*phenetidine*, $OEt\cdot C_6H_4\cdot NMe_2$, is obtained as a colourless oil by the action of hot methyl sulphate on *o*-phenetidine. It boils at 218—220°, has a characteristic odour, and becomes pink in the light. Concentrated nitric acid converts it into Blanksma's 3 : 5-dinitromethylnitroamino-*o*-phenetidine (Abstr., 1905, i, 431), from which phenol removes the *N*-nitro-group, producing 3 : 5-dinitromonomethyl-*o*-phenetidine (Blanksma, *loc. cit.*). This secondary amine yields with nitrous acid, 3 : 5-*dinitromethylnitrosoamino*-o-*phenetidine*,

$$OEt\cdot C_6H_2(NO_2)_2\cdot NMe\cdot NO,$$

which crystallises from alcohol in yellow needles, m. p. 71°. The nitroamine forms a green solution in a little cold sulphuric acid, giving the same nitrosoamine (20% yield), accompanied by a small quantity of the dinitromethyl-*o*-phenetidine, only the latter being recovered when excess of acid is used, or the temperature is allowed to rise. Methyl sulphate also methylates *p*-phenetidine, yielding Knorr's dimethyl-*p*-phenetidine (Abstr., 1897, i, 108), which cold concentrated nitric acid converts into 3 : 5-*dinitromethylnitroso*-p-*phenetidine*, $OEt\cdot C_6H_2(NO_2)_2\cdot NMe\cdot NO$. This separates in shining leaflets, m. p. 108°, and is oxidised by fuming nitric acid to 3 : 5-*dinitromethylnitroamino*-p-*phenetidine*, $OEt\cdot C_6H_2(NO_2)_2\cdot NMe\cdot NO_2$, which crystallises in pale yellow needles from alcohol, m. p. 95°, and furnishes with phenol, 3 : 5-*dinitromethyl*-p-*phenetidine*,

$$OEt\cdot C_6H_2(NO_2)_2\cdot NHMe,$$

in jagged, dark red crystals, m. p. 98°, the position of the nitro-groups being confirmed by the formation of a *m*-diamine. The nitroamine dissolves in cold sulphuric acid with an intense red colour, yielding the nitrosoamine; these characteristic colours serve to detect the presence of small traces of nitroamines in impure nitrosoamines. J. C. W.

A New Method of Preparing Thiocarbimides. LUDWIG KALUZA (*Monatsh*, 1912, 33, 363—371. Compare Andreasch, Abstr., 1907, 1, 233; Kalaza, Abstr., 1910, i, 130).—Good yields of thiocarbimides are obtained by the interaction of ethyl chloroformate and the potassium or ammonium salts of alkyl (or aryl) dithiocarbamic acids. Symmetrical di-substituted carbamides are formed at the same time, the removal of which is impossible in certain cases.

Methylthiocarbimide, m. p. 35°, b. p. 118°, and ethylthiocarbimide were obtained in yields of 78—85% by the interaction of ethyl chloroformate with potassium methyldithiocarbamate and potassium ethyldithiocarbamate respectively. In each case, only traces of the corresponding carbamide derivatives were present. Phenylthiocarbimide and *o*- and *p*-tolylthiocarbimides were similarly prepared, but contained 12—25% of disubstituted carbamide derivatives, from which they could not be satisfactorily separated. In the cases of the tolylthiocarbimides these impurities were identified as di-*o*-tolylcarbamide, m. p. 251°, and di-*p*-tolylcarbamide, m. p. 263°. Andreasch (*loc. cit.*) has shown that phenylthiocarbimide deposits diphenylcarbamide.

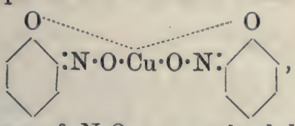
[With R. HAID.]—*o*-Anisylthiocarbimide was readily obtained from ethyl chloroformate and ammonium *o*-anisyldithiocarbamate. It deposits di-*o*-anisylcarbamide when preserved for some time.

a-Naphthylthiocarbimide, m. p. 58°, and *β-naphthylthiocarbimide*, m. p. 62—63°, were similarly obtained in yields of 85—86% and 88% respectively. The small amounts of *s*-dinaphthylcarbamide simultaneously formed were readily removed by recrystallisation from alcohol. H. W.

Catalysis of Cyclic Alcohols by the Wet Way by means of Sulphuric Acid; Preparation of *cyclo*Hexenes. JEAN B. SENDERENS (*Compt. rend.*, 1912, 154, 1168—1170. Compare this vol., i, 331).—*cyclo*Hexanol and its homologues may be converted into the corresponding unsaturated hydrocarbons by distillation with 3—4% of their volume of sulphuric acid. The yields are not so good as those obtained in the dry way, but the method is more convenient. *cyclo*-Hexanol gave 89% of the theoretical yield of hydrocarbon.

On distilling menthol with 1—2% of its volume of sulphuric acid, menthene was obtained in the same yield as that given by the dry catalytic method (compare this vol., i, 406). As the use of 4—5% of the acid, diluted with twice its volume of water, does not diminish the yield, it would appear that the process is strictly catalytic and does not depend on absorption of water by the acid. Anhydrous aluminium sulphate, a good catalyst for menthol in the dry way, is inefficient in the wet method. W. O. W.

***o*-Nitrosophenol.** OSKAR BAUDISCH and NIKOLAUS KARZEFF (*Ber.*, 1912, 45, 1164—1171).—*o*-Nitrophenol was converted into *o*-nitrophenyl *p*-toluenesulphonate, and this reduced by means of hydrogen sulphide and ammonia to the corresponding hydroxylamine compound, which was converted by means of amyl nitrite and ammonia into the ammonium salt of the corresponding nitrosohydroxylamine compound, $C_7H_7{\cdot}SO_2{\cdot}O{\cdot}C_6H_4{\cdot}N(NO){\cdot}O{\cdot}NH_4$. On hydrolysis with boiling sodium hydroxide, sodium *o*-hydroxy-*m*-nitrosophenylhydroxylamine, $OH{\cdot}C_6H_4{\cdot}N(NO){\cdot}ONa$, is formed. This forms an internally complex copper salt, $\left(OH{\cdot}C_6H_4{\cdot}N{<}{}^{NO-}_{-O-}{>}\right)_2Cu$, which dissolves in organic solvents with a bluish-green coloration and crystallises from acetone in pale grey needles. In presence of traces of acid, it becomes deep red, and on precipitation of the red solution with light petroleum an almost black, crystalline precipitate is obtained of a salt:



Reddish-brown fumes of N_2O_3 are evolved during the transformation of the grey into the red copper salt. The *calcium* salt corresponding with the red salt consists of a deep red crust with a strong greenish-gold reflex, and gives a deep red solution in water. When this is extracted with light petroleum after being made acid with metaphosphoric acid, an emerald-green extract is obtained, which on

evaporation leaves greenish-yellow needles of *o*-nitrosophenol. These have a strong odour, and are very volatile. The *iron* salt forms lustrous, greenish-black crystals; the *cobalt* salt is almost black, but gives red solutions.

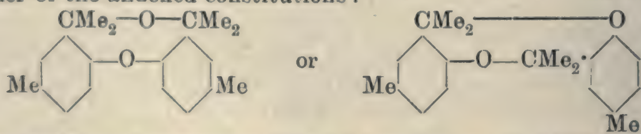
o-Nitrosophenol is more quickly prepared by oxidation of *o*-hydroxylaminophenyl *p*-toluenesulphonate with silver oxide to *o*-nitrosophenyl *p*-toluenesulphonate, which exists in green and colourless modifications, the green form being labile. On boiling with calcium hydroxide, the calcium salt of *o*-nitrosophenol is formed.

o-*Hydroxylaminophenyl* p-*toluenesulphonate* crystallises in snow-white needles, m. p. 112·5°.

The *ammonium* salt of o-*nitrosohydroxylaminophenyl* p-*toluenesulphonate* has m. p. 119°; it becomes yellow and dirty brown on exposure to the air for a few hours. When decomposed with metaphosphoric acid, o-*nitrosohydroxylaminophenyl* p-*toluenesulphonate*, $C_6H_4Me\cdot SO_2\cdot O\cdot C_6H_4\cdot N(NO)\cdot OH$, is obtained in colourless crystals, m. p. 76·5°.

o-*Nitrosophenyl* p-*toluenesulphonate* forms green crystals, m. p. 45°, and colourless, lustrous needles, m. p. 87·5—88·5°. E. F. A.

Condensation Products of *m*- and *p*-Cresol with Acetone. THEODOR ZINCKE and W. GAEBEL (*Annalen*, 1912, **388**, 299—312).—The condensation of *o*-cresol with acetone is similar to that of phenol; the product, on account of its behaviour with bromine, doubtless has the constitution $CMe_2(C_6H_3Me\cdot OH)_2$. When a mixture of *m*- or *p*-cresol (six parts) and acetone (one part) is saturated with hydrogen chloride in the cold, and is heated at 100° for thirty hours, or when the mixture is heated on the water-bath for a long time with phosphoryl chloride (0·1 part), condensation products are obtained, which are probably ethers on account of their chemical indifference and insolubility in alkalis. The condensation product from *m*-cresol is identical with the substance obtained by the action of hydriodic acid on hydroxythymol (Fries and Fickewirth, Abstr., 1908, i, 822); it is dimorphous, crystallising from alcohol in monoclinic prisms, m. p. 132°, and from glacial acetic acid in rhombic plates, m. p. 126°. The condensation product of *p*-cresol and acetone, which probably has one or other of the annexed constitutions:



is likewise dimorphous, crystallising in needles, m. p. 138°, or plates, m. p. 144°.

When heated with phosphorus pentachloride at 130°, both condensation products yield amorphous, yellowish-white powders having approximately the composition $C_{20}H_{16}O_2Cl_8$; the m. p. of the meta-derivative is 90—110°, that of the para-derivative, 73—85°. By chlorination in the presence of iron, the condensation product of *m*-cresol and acetone yields an impure *tetrachloro*-derivative, m. p. 198—201°, in glacial acetic acid, and a *hexachloro*-derivative, $C_{20}H_{18}O_2Cl_6$, m. p. 208° in chloroform. Under similar conditions, the condensation

product of *p*-cresol yields in either solvent an *octachloro*-derivative, m. p. 105—115°, which is probably identical with the preceding. By bromination, the condensation product of *m*-cresol forms an impure *tetrabromo*-derivative, m. p. 190°, or a *hexabromo*-derivative, m. p. 252°, whilst the condensation product of *p*-cresol yields an impure *dibromide*, m. p. 213°, or *hexabromo*-derivative, m. p. 300° (decomp.). The reduction of the condensation products by zinc dust at 320—350° yields a gas (probably propane), *m*- or *p*-cresol, and *substances*, $C_{10}H_{14}O$, b. p. 230—240° and 240—250° respectively, which are probably tertiary alcohols, $OH\cdot CMe_2\cdot C_6H_4Me$.

Oxidation of the condensation products by chromic acid yields definite results only in the case of the para-derivative. In this case an *acid*, $C_{20}H_{20}O_6$, m. p. above 270°, white needles, is obtained; the *sodium*, *barium*, and *silver* salt, and the *methyl* and *ethyl* esters, m. p. 215° and 180° respectively, are described. C. S.

A New Synthesis of Hordenine. HUGO VOSWINCKEL (*Ber.*, 1912, **45**, 1004—1006).—Hordenine, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2$, can be synthesised (compare Barger, Trans., 1909, **95**, 2193; Rosenmund, Abstr., 1910, i, 241) by the following steps which provide a general process for the synthesis of hydroxyphenylethylamine bases.

p-*Methoxyphenyl dimethylaminomethyl ketone*,

$$OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot NMe_2,$$

is prepared by the action of an alcoholic solution of dimethylamine on *p*-methoxyphenyl chloromethyl ketone (Kunckell and Johannsen, Abstr., 1897, i, 522); it forms a colourless oil, m. p. about 30°. The *hydriodide* (colourless needles, m. p. 150°) on boiling with hydriodic acid (D 1·7) and phosphorus gives p-*hydroxyphenyl dimethylaminomethyl ketone*, colourless, prismatic crystals, m. p. 142°; the *hydriodide* of this base (needles, m. p. 176°) when heated in a sealed tube with hydriodic acid (D 1·96) and phosphorus gives hordenine (m. p. 118°; methiodide, m. p. 228—229°). D. F. T.

Preparation of *p*-Hydroxyphenyl*iso*propylamine. KARL W. ROSENMUND, CARL MANNICH, and WILLY JACOBSOHN (D.R.-P. 243546). —p-*Methoxyphenyl*iso*propylamine*, $OMe\cdot C_6H_4\cdot CH_2\cdot CHMe\cdot NH_2$, a strongly basic oil, b. p. 158°/25 mm., is readily prepared by reducing *p*-methoxybenzyl methyl ketoxime, $OMe\cdot C_6H_4\cdot CH_2\cdot CMe{:}NOH$, with sodium amalgam; the *hydrochloride*, colourless leaflets, has m. p. 210°. When the foregoing base is boiled during fifteen minutes with three parts of hydriodic acid (D 1·7), it furnishes p-*hydroxyphenyl*iso*propylamine hydriodide*, m. p. 155°; this *base* forms colourless rosettes, has m. p. 125—126°, and is of therapeutic value. F. M. G. M.

Constitution of the Bromides of *p*-*iso*Propylphenol and *p*-*sec* Butylphenol. THEODOR ZINCKE (*Annalen*, 1912, **388**, 294—298). —The constitutions ascribed to the hexa- and heptabromo-derivatives of *p*-*iso*propylphenol obtained by the action of bromine on 3 : 5 : 3′ : 5′-tetrabromo-*p*-diphenoldimethylmethane (Abstr., 1906, i, 172) were given to these substance in consequence of the constitution given by Baeyer and Seuffert to the hexabromothymol obtained from menthone (Abstr., 1901, i, 216). Since, however, Fries has shown (Abstr., 1910, i, 333) that the hexabromothymol contains only two bromine atoms in

the nucleus, the constitutions of the hexa- and the heptabromo-derivatives of *p-iso*propylphenol become open to doubt. It is now shown that the hexabromo-*p-iso*propylenephenol obtained from the acetylated heptabromide (*loc. cit.*) yields with alkali and methyl sulphate a *methyl ether*, $OMe\cdot C_6H_2Br_2\cdot C(CHBr_2)\colon CBr_2$, m. p. 127°, which is oxidised to 3 : 5-*dibromo*-4-*methoxybenzoic acid*, m. p. 213°, by boiling nitric acid, D 1·4, and water (2 : 3 by volume). The heptabromide, therefore, probably has the constitution

$$OH\cdot C_6H_2Br_2\cdot CBr(CHBr_2)_2,$$

whilst the hexabromide is represented by

$$OH\cdot C_6H_2Br_2\cdot CBr(CHBr_2)\cdot CH_2Br.$$

The constitutions previously ascribed to the hexa- and heptabromo-derivatives of *p-sec*-butylphenol (Abstr., 1908, i, 780) must be altered in a corresponding manner; the hexabromide probably has the constitution $OH\cdot C_6H_2Br_2\cdot CBr(CHBr_2)\cdot CHMeBr$, and the heptabromide the constitution $OH\cdot C_6H_2Br_2\cdot CBr(CHBr_2)\cdot CMeBr_2$. C. S.

Amidosulphonic Acid. Karl A. Hofmann and E. Biesalski (*Ber.*, 1912, **45**, 1394—1398).—The authors recommend the employment of amidosulphonic acid as a standard in acidimetry. Its gradual hydrolysis in aqueous solution to acid ammonium sulphate has little influence on most titrations.

It may also be used in the preparation of aryl-sulphuric acids and phenol-sulphonic acids, and possesses the advantage over sulphuric acid that no separation of the product from excess of sulphonating agent is necessary. Thus ammonium phenol-*p*-sulphonate results when phenol is heated with amidosulphonic acid at 150—160°, whilst at 100° ammonium phenyl sulphate is obtained. From the above it might appear that the latter compound is formed as an intermediate step in the preparation of ammonium phenol-*p*-sulphonate. Against this view, however, is the fact that ammonium anisole-*p*-sulphonate is obtained in good yield when anisole and amidosulphonic acid are heated at 140—150° during six hours. Similarly, *o*-, *m*-, and *p*-cresols, and 1 : 2 : 4- and 1 : 3 : 4-xylenols are sulphonated by amidosulphonic acid at 150°. β-Naphthol at 160° is similarly transformed into ammonium 2-naphthol-6-sulphonate.

In all these cases no dehydrating agent is necessary, since the eliminated water is absorbed in the hydrolysis of the amino-group with the formation of an ammonium salt. This intramolecular redistribution of water is particularly obvious when amidosulphonic acid is brought into contact with the carbinol base of malachite-green, whereupon the dye is at once produced. H. W.

***o*-Hydroxytolylsulphone.** Josef Zehenter (*Monatsh.*, 1912, **33**, 333—347).—*o*-Hydroxytolylsulphone was obtained in good yield by heating *o*-cresol (2 parts) with sulphuric acid containing 8% sulphur trioxide (1 part) during three to four hours at 160—180°. It separates from alcohol in colourless prisms, m. p. 263—265°. Its identity with the compound prepared by Tassinari (Abstr., 1889, 245) follows from its m. p., and that of its diacetyl derivative. Salts of it could not be prepared, nor could any definite oxidation product be isolated. Its constitution has not been proved, but the $\cdot SO_2$ group is in the ortho- or para-position to the hydroxyl group. *o*-Cresol-

p-sulphonic acid was isolated as by-product in the above reaction, and its potassium and barium salts were analysed.

Bromine in hot ethereal solution transforms *o*-hydroxytolylsulphone into *dibromo-o-hydroxytolylsulphone*, $C_{14}H_{12}O_4Br_2S$, m. p. 254—256°, whilst, in the absence of a solvent, tetrabromo-*o*-cresol, m. p. 207—208°, is formed. When heated on the boiling water-bath with nitric acid (D 1·2), *o*-hydroxytolylsulphone yields *dinitro-o-hydroxytolylsulphone*, $C_{14}H_{12}(NO_2)_2O_4S$, m. p. 243°, the *potassium* salt of which,

$$C_{14}H_{10}(NO_2)_2O_4SK_2,3{\cdot}5H_2O,$$

was analysed. At the ordinary temperature, concentrated sulphuric acid converts *o*-hydroxytolylsulphone mainly into *o*-cresol-3-sulphonic acid [isolated in the form of its barium salt, $(OH{\cdot}C_6H_3Me{\cdot}SO_3)_2Ba,3H_2O$], which when oxidised with nitric acid forms 3 : 5-dinitro-*o*-cresol, m. p. 85·5°; at 100—110°, this acid together with *o*-cresol-3 : 5-disulphonic acid is formed, whilst at 160—170° practically only the latter acid is obtained. Its potassium and barium salts were analysed. Oxidation with concentrated nitric acid converts the potassium salt into 3 : 5-dinitrocresol. H. W.

The Ferric Chloride Reaction with Catechol. II. Violet Iron-Catechol Compounds. RUDOLF FRIEDRICH WEINLAND and KARL BINDER (*Ber.*, 1912, 45, 1113—1124).—The authors have already shown (Abstr., 1912, i, 184) that the deep red solutions formed when ferric salts and catechol are mixed in alkaline solution contain the salts of on acid, $H_3[Fe^{III}(C_6H_4O_2)_3]$. These solutions when diluted become reddish-violet and then violet, and contain salts of a new acid, $H[Fe(C_6H_4O_2)_2]$. Aqueous solutions of salts of the red acid have an alkaline reaction, and are hydrolysed according to the equations:

$$K_3[Fe^{III}(C_6H_4O_2)_3] + 2H_2O = KH_2[Fe^{III}(C_6H_4O_2)_3] + 2KOH$$
$$KH_2[Fe^{III}(C_6H_4O_2)_3] = K[Fe(C_6H_4O_2)_2] + C_6H_4(OH)_2.$$

The ammonium salts of the violet acid may be obtained by boiling a dilute aqueous solution of the ammonium salt of the red acid, since the liberated ammonia is volatilised. In the case of non-volatile bases, the addition of acetic acid is necessary. Salts of the violet acid may also be prepared by mixing solutions of catechol, ferric acetate, and alkali acetate.

The free violet acid and its salts are black, microcrystalline substances, soluble in water, insoluble in alcohol. All contain water, which, in the case of the normal potassium salt, was retained after preservation in a vacuum over sulphuric acid during four weeks. Their aqueous solutions are immediately decolorised by the addition of mineral acids, whilst addition of alkali results in the formation of salts of the red acid, one-third of the iron being precipitated as ferric hydroxide. In certain circumstances, the addition of acetic acid to the solutions of normal salts of the red acid causes the formation of acid salts of the same acid, which consist of brownish-black or black, crystalline powders soluble in water or alcohol with the formation of violet solutions. Alkali dissolves them with formation of red solutions and without precipitation of ferric hydroxide.

The free violet *acid*, $H\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right],H_2O$, was obtained as a black

powder, sparingly soluble in water or alcohol, by mixing aqueous solutions of catechol, ferric acetate, and sodium acetate.

The *sodium dihydrogen* salt of the red acid,

$$NaH_2[Fe^{III}(C_6H_4O_2)_3],3H_2O,$$

prepared by the addition of one or two equivalents of acetic acid to the normal sodium salt of the red acid and evaporation of the solution over sulphuric acid, is readily transformed into the *normal sodium* salt of the violet acid, $Na\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right]$, by evaporating its aqueous solution on the water-bath. By the action of three equivalents of acetic acid on the normal sodium salt of the red acid, an *acid sodium* salt of the violet acid was obtained as a black powder.

The *normal potassium* salt of the violet acid, $K\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right]$, was prepared by addition of one or two equivalents of acetic acid to a solution of the normal potassium salt of the red acid. The *acid potassium* salt of the violet acid,

$$2K\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right] + H\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right] + 2H_2O,$$

was formed when three equivalents of acetic acid were used.

The *normal ammonium* salt of the violet acid, $NH_4\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right]$, was obtained on evaporating a solution of the normal ammonium salt of the red acid. The latter, when treated with three equivalents of acetic acid, yielded an *acid ammonium* salt of the violet acid,

$$2NH_4\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right] + H\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right] + 3H_2O.$$

A second *acid ammonium* salt of the violet acid,

$$NH_4\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right] + H\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right] + 2{\cdot}5H_2O,$$

was obtained by mixing solutions of catechol, ammonium acetate, and ferric acetate. When larger quantities of ammonium acetate were employed (7—12 equivalents instead of 3·5), an *ammonium* salt of the red and violet acid, $4NH_4\left[\begin{matrix}Fe(C_6H_4O_2)_2\\H_2O\end{matrix}\right] + (NH_4)_3[Fe^{III}(C_6H_4O_2)_3] + (NH_4)_2H[Fe^{III}(C_6H_4O_2)_3] + 13H_2O$, was obtained. From the mother liquor left in this experiment, the *diammonium hydrogen* salt of the red acid, $(NH_4)_2H[Fe^{III}(C_6H_4O_2)_3],4H_2O$, was prepared. H. W.

A Contribution to the Knowledge of Phloroglucinol. A. Göschke and Josef Tambor (*Ber.*, 1912, **45**, 1237, 1239).—Although resacetophenone, quinacetophenone, and gallacetophenone are now easily obtainable hydroxy-ketones, 2 : 4 : 6 - trihydroxyacetophenone or phloroacetophenone has not yet been synthesised. Many flavone and flavonol colouring matters possess the same carbon skeleton, and recently Semmler and Schossberger have found its dimethyl ether in some ethereal oils (Abstr., 1911, i, 1002), whilst Rupe has suggested that cyanomaclurin may be a pentahydroxychalkone, that is, a condensation product of phloroacetophenone and resorcinaldehyde. As the present authors have found that polyhydroxychalkones are coloured (compare Abstr., 1912, i, 30), whereas cyanomaclurin is a

colourless powder, they have attempted to apply Nencki's method (Abstr., 1899, 879) to the synthesis of phloroacetophenone. Two substances have been obtained, but they proved to be the triacetyl*cyclo*hexantrione (Abstr., 1909, i, 656) and diacetyl*cyclo*hexantrione (Abstr., 1912, i, 274) of Heller. From the former an as-*phenylmethylhydrazone*, $C_{15}H_{16}O_3N_2$, has been obtained in very small, yellow prisms, m. p. 165°. Further studies on the action of acid chlorides on phloroglucinol and on aromatic hydroxy-acids are in progress.

J. C. W.

3-Methoxy-4 : 5-methylenedioxybenzylamine. LEOPOLD RÜGHEIMER and G. RITTER (*Ber.*, 1912, 45, 1340—1343).—Myristicinaldehyde (Semmler, Abstr., 1891, 311) was converted into the *oxime* (m. p. 159—160°), which could be reduced by zinc dust and acetic acid to 3-*methoxy*-4 : 5-*methylenedioxybenzylamine*,

$$OMe\cdot C_6H_2(\colon O_2\colon CH_2)\cdot CH_2\cdot NH_2,$$

a strong base, b. p. 172·5°/16·5 mm.; *hydrochloride*, m. p. 222°, gives solutions with green fluorescence; *double* salt with mercuric chloride, needles, m. p. 215°; *platinichloride*, yellow needles and leaflets; *picrate*, leaflets.

The acetal compound, $OMe\cdot C_6H_2(\colon O_2CH_2)\cdot CH_2\cdot NH\cdot CH_2\cdot CH(OEt)_2$, unlike that of 3 : 4-dimethoxybenzylamine (compare Rügheimer and Schön, Abstr., 1908, i, 153; 1909, i, 605), does not condense to an *iso*quinoline derivative.

The amine reacts with phenylcarbimide, giving *phenyl*-3-*methoxy*-4 : 5-*methylenedioxybenzylcarbamide*, $(C_9H_9O_3)NH\cdot CO\cdot NHPh$, slender needles, m. p. 174°; phenylthiocarbimide similarly gives the corresponding *thiocarbamide*, plates, m. p. 143°. It readily condenses with acetylacetone, giving *β*-3-*methoxy*-4 : 5-*methylenedioxybenzyliminopropyl methyl ketone*, $CMe[\colon N\cdot CH_2\cdot C_6H_2(\colon O_2CH_2)\cdot OMe]CH_2\cdot CO\cdot CH_3$, m. p. 73°.

D. F. T.

Derivatives of 3 : 4 : 5 : 3′ : 4′ : 5′-Hexahydroxydiphenyl. CARL LIEBERMANN and E. HERRMUTH (*Ber.*, 1912, 45, 1218—1227).—Hexahydroxydiphenyl is readily converted by oxidising agents into the bluish-violet sparingly soluble tetrahydroxydiphenoquinone. 2 : 6 : 2′ : 6′-Tetrabromohexahydroxydiphenyl, however, cannot be oxidised to the corresponding quinone.

The possibility of the molecule being half the size, namely, $C_6HBr_2(OH)_3$, is discussed; it is shown that it is not identical with dibromopyrogallol, and that the resistance to oxidation is due to the influence of the substituting groups.

Dihydroxydicarbonatodiphenyl,

$$CO<\substack{O\\O}>C_6H_2(OH)\cdot C_6H_2(OH)<\substack{O\\O}>CO,$$

forms slender needles, m. p. 312° (decomp.).

Hexa-acetoxydiphenyl, $C_{12}H_4(OAc)_6$, crystallises in colourless needles, m. p. 236° (previously given 145°).

Tetrahydroxydiphenoquinone, prepared by the action of alcoholic iodine solution on the aqueous solution of hexahydroxydiphenyl, is obtained as a deep blue precipitate, dissolving in concentrated sulphuric acid with a brown coloration.

Tetrabromohexa-acetoxydiphenyl, $C_6Br_2(OAc)_3 \cdot C_6Br_2(OAc)_3$, crystallises in platelets, m. p. 231°. On hydrolysis, *tetrabromohexahydroxydiphenyl* is obtained in colourless leaflets, which darken at 260°, m. p. 270—276° (decomp.). The solution in dilute alkali is at first colourless; it becomes red at the surfaces of contact with the air, and finally a deep red all through.

Dibromopyrogallol as prepared either by Einhorn (Abstr., 1904, i, 238) or by Perkin and Simonsen (Trans., 1905, 87, 863) has m. p. 158° (decomp.); the acetate has m. p. 143°, and shows other differences in its behaviour from tetrabromohexahydroxydiphenyl.

E. F. A.

Optically Active Phenylmethylcarbinols. Bror Holmberg (*Ber.*, 1912, 45, 997—1003).—In order to discover, if possible, any directing influence in the Walden inversion exerted by the groups already attached to the asymmetric atom, the author has selected for investigation *a*-phenylethyl alcohol as a structurally simple substance.

a-Phenylethylamine was prepared from acetophenoneoxime and then resolved (compare Lovén, Abstr., 1905, i, 875); the *l*-form has D_4^{20} 0·952; the two forms had a_D^{19} + and − 38·73° respectively, and b. p. 77—77·5°/16 mm. (compare Markwald and Meth, Abstr., 1905, i, 272).

Treatment of the *l*-form with sulphuric acid and sodium nitrite gave *a*-phenylethyl nitrite, an unstable, yellow oil, b. p. 72·5—73°/19 mm., D_4^{20} 1·045, a_D^{17} + 6·80°, together with *a*-phenylethyl alcohol, a colourless liquid, b. p. 98·5—99°/20 mm., D_4^{20} 1·018, a_D^{15} + 5·00° (compare Emmerling and Engler, this Journ., 1874, 74; Marckwald and Meth, *loc. cit.*). The *d*-base on similar treatment, but with less careful cooling, gave the stereoisomeric *l*-alcohol and nitrite, of similar properties to the enantiomorphs, but with lower optical activity, evidently due to partial racemisation.

d-*a*-Phenylethyl alcohol was converted by hydrogen bromide into the bromide, b. p. 94·5°/19 mm., D_4^{20} 1·311 (compare Bernthsen and Bender, Abstr., 1883, 70); the product was completely inactive. The action of phosphorus pentabromide on an ethereal solution of the *l*-alcohol produced a feebly *d*-bromide, whilst the action of nitric oxide and bromine on the hydrobromide of *d*-*a*-phenylethylamine gave a very small quantity of a *d*-liquid (presumably the bromide ester).

When *d*-phenylethyl bromide was treated in alcoholic solution with moist silver oxide, *phenylethyl ethyl ether* was produced, b. p. 71·5—72°/15 mm., a_D^{15} − 0·20°, and also a smaller amount of another lævorotatory substance, apparently *a*-phenylethyl alcohol.

D. F. T.

Preparation of Phenyl-, Alkyloxyphenyl-, and Dialkyloxyphenyl-ethanolamines and their Alkyl Ethers. Karl W. Rosenmund (D.R.-P. 244321. Compare Abstr., 1911, i, 34).—Compounds having the general formula $R \cdot CH(OR_1) \cdot CH_2 \cdot NH_2$ (where R is phenyl, alkyloxyphenyl, or dialkyloxyphenyl, and R_1 hydrogen or an alkyl group) are readily prepared by the condensation of benzaldehyde (or its alkyloxy- or dialkyloxy-substitution products)

with nitromethane in the presence of alkali and subsequent reduction of the nitro-group.

β-Hydroxy-β-phenylethylamine, $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NH_2$, is obtained by treating a cooled alcoholic mixture of benzaldehyde and nitromethane with sodium ethoxide (1·5 mols.), followed by reduction with sodium amalgam. The *hydrochloride* is an oil; the intermediate nitro-alcohol, an oil, has b. p. 164—167°/20 mm., with partial decomposition.

a-Nitro-β-methoxy-β-phenylethane, $OMe{\cdot}CHPh{\cdot}CH_2{\cdot}NO_2$, an oil, b. p. 140—141°/15 mm., is prepared in a similar manner from nitrostyrene in methyl-alcoholic solution, and on reduction furnishes *β-methoxy-β-phenylethylamine*, which was isolated in the form of its crystalline *hydrochloride*, m. p. 158—159°.

β-Hydroxy-β-p-*methoxyphenylethylamine*,

$$OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH_2{\cdot}NH_2,$$

obtained from anisaldehyde and nitromethane, was isolated as its *hydrochloride*, m. p. 168—173°.

β-Methoxy-β-p-*methoxyphenylethylamine*,

$$OMe{\cdot}C_6H_4{\cdot}CH(OMe){\cdot}CH_2{\cdot}NH_2,$$

prepared from *p*-methoxynitrostyrene, furnishes a *hydrochloride*, m. p. 165—166·5°, decomp. 186—187°.

β-Nitrodimethoxystyrene (*loc. cit.*) is converted by the action of sodium methoxide into the corresponding *a-nitro-β-methoxy-β*-3 : 4-*dimethoxyphenylethane*, an unstable, yellow oil, which on reduction furnishes *β-methoxy-β*-3 : 4-*dimethoxyphenylethylamine*,

$$C_6H_3(OMe)_2{\cdot}CH(OMe){\cdot}CH_2{\cdot}NH_2;$$

its *hydrochloride* has m. p. 182—183°. F. M. G. M.

Dehydration of Diphenyl-ψ-butylcarbinol. (Mme.) PAULINE RAMART-LUCAS (*Compt. rend.*, 1912, **154**, 1088—1090. Compare Abstr., 1911, i, 636).—The tertiary alcohol, $C_{17}H_{20}O$, previously described behaves normally with thionyl chloride, giving a *chloride*, $C_{17}H_{19}Cl$, m. p. 72—73°, but yields an *isomeride* of this substance, m. p. 109°, when treated with acetic anhydride and acetyl chloride; dehydration also occurs, however, with production of benzophenone and β-methylpropane. Oxidation of the alcohol with chromic acid, leads to the formation of carbon dioxide, acetophenone, and benzophenone, whilst the corresponding unsaturated hydrocarbon, $C_{17}H_{18}$, under the same conditions yields the same substances together with an *acid*, crystallising in needles, m. p. 173°. The constitution of the hydrocarbon cannot be settled without a further examination of this oxidation product. W. O. W.

The Behaviour of Some Degradation Products of Cholesterol on Heating. ADOLF WINDAUS (*Ber.*, 1912, **45**, 1316—1321).—On account of the stability of the structure of cholesterol towards heat (compare Diels and Linn, Abstr., 1908, i, 164, 263), it is probable that many reactions occurring at elevated temperatures may provide trustworthy evidence as to the constitution of this substance.

The dibasic acid, $C_{27}H_{44}O_4$ (Diels and Abderhalden, Abstr., 1904, i, 880), when covered with acetic anhydride, the mixture distilled under ordinary pressure, and the residue under reduced pressure, loses carbon dioxide and water with the formation of a cyclic *ketone*,

$C_{26}H_{42}O$, needles, m. p. 95—96°; *oxime*, m. p. 176°. This behaviour indicates that in the original acid the two carboxyl groups must be in a 1 : 6- or 1 : 7-position to each other.

The tribasic acid, $C_{25}H_{40}O_6$, obtained from the previous acid (Windaus, Abstr., 1908, i, 264, 728; 1909, i, 920) under similar treatment loses carbon dioxide and water with the formation of a cyclic ketonic carboxylic acid, $C_{24}H_{38}O_3$, which separates from dilute acetic acid in hexagonal tablets, m. p. 146—147°; *semicarbazone*, leaflets, m. p. 249—250° (decomp.). From analogy to the conversion of homocamphoronic acid into camphononic acid (Lapworth and Chapman, Trans, 1899, 75, 986), the disappearing carboxyl groups must likewise be in the 1 : 6- or 1 : 7-position.

The acid, $C_{24}H_{38}O_3$, on oxidation with chromic acid in acetic acid solution gives a tricarboxylic *acid*, $C_{24}H_{38}O_6$, slender, prismatic crystals containing water of crystallisation, m. p. (anhydrous) 216°; the *sodium* salt is sparingly soluble. An isomeric *acid*, m. p. *ca.* 201°, is simultaneously produced. By comparison of this behaviour with that of camphononic acid (Lapworth and Chapman, *loc. cit.*), the carbonyl group in the acid, $C_{24}H_{38}O_3$, must be adjacent to a $-CH_2$ group.

The acid, $C_{24}H_{38}O_6$, when subjected to similar distillation produces (with loss of water and carbon dioxide) a cyclic ketonic *acid*, $C_{23}H_{36}O_3$, thin, prismatic crystals from acetic acid, m. p. 170°; *semicarbazone*, leaflets, m. p. 226° (decomp.). D. F. T.

Preparation of Chloro-substituted Derivatives of Anthranilic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 244207. Compare Trans., 1902, 81, 1324).—When polychlorobenzoic acids are heated at 100—150° during twelve to fifty hours with 30% ammonium hydroxide in the presence of copper, the chlorine atom in the ortho-position to the carboxyl group is replaced by an amino-group.

4-Chloro-2-aminobenzoic acid was thus obtained in quantitative yield from 2 : 4-dichloro-benzoic acid, whilst 2 : 4 : 5-trichlorobenzoic acid furnished 4 : 5-*dichloro-2-aminobenzoic acid*, colourless needles, m. p. 210° (approx.). F. M. G. M.

***p*-Aminobenzonitrile and Certain of its Derivatives. III.** MARSTON T. BOGERT and LOUIS ELSBERG WISE (*J. Amer. Chem. Soc.*, 1912, 34, 693—702).—An account is given of a continuation of the study of derivatives of *p*-aminobenzonitrile (Bogert and Kohnstamm, Abstr., 1903, i, 559; Bogert and Wise, Abstr., 1911, i, 46).

p-Aminobenzonitrile *picrate*, m. p. 150·5° (corr.), forms long, silky, golden-yellow needles. p-*Nitrobenzoyl*-p-*aminobenzonitrile*,

$$NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CN,$$

m. p. 258—259° (uncorr.), obtained by the action of *p*-nitrobenzoyl chloride on *p*-aminobenzonitrile, crystallises in long, pale yellow, lustrous needles. p-*Cyanophenylurethane*, $CN\cdot C_6H_4\cdot NH\cdot CO_2Et$, m. p. 116—117° (corr.), prepared by treating *p*-aminobenzonitrile with ethyl chloroformate in presence of sodium carbonate, forms colourless needles with a faint, pineapple-like odour, and when heated with hydrogen peroxide solution is converted into p-*carbamylphenylurethane*,

$$NH_2\cdot CO\cdot C_6H_4\cdot NH\cdot CO_2Et,$$

m. p. about 232·5° (uncorr.), which crystallises in slender, colourless, silky needles. p-*Cyanophenylcarbamide*, $CN\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2$, m. p. 207·5—208·5° (uncorr.), from *p*-aminobenzonitrile hydrochloride and potassium cyanate, forms minute, colourless needles. p-*Cyanocarbanilide*, $CN\cdot C_6H_4\cdot NH\cdot CO\cdot NHPh$, m. p. 198·5° (corr.), obtained by the action of phenylcarbimide on *p*-aminobenzonitrile, crystallises in clusters of colourless, silky needles. *Di*-p-*cyanocarbanilide*,

$$(CN\cdot C_6H_4\cdot NH)_2CO,$$

m. p. 273° (uncorr.), from *p*-aminobenzonitrile and carbonyl chloride, forms small, colourless needles.

When ethyl *p*-cyano-oxanilate is heated with concentrated solution of ammonia, it is converted into p-*cyano-oxanilamide*,

$$CN\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH_2,$$

m. p. above 300°, which forms minute, colourless crystals. p-*Cyano-oxanilanilide*, $CN\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NHPh$, m. p. 246° (uncorr.), obtained by the action of aniline and zinc chloride on ethyl *p*-cyano-oxanilate, forms small, colourless crystals.

p-*Cyanosuccinanilic acid*, $CN\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 213—214° (uncorr.), obtained by the action of succinic anhydride on *p*-aminobenzonitrile, crystallises in minute, colourless prisms; its *methyl* and *ethyl* esters have m. p. 155—156° (corr.) and 111° (corr.) respectively; the *silver* salt is described. The *anil*,

$$CN\cdot C_6H_4\cdot N{<}{\begin{array}{l}CO\cdot CH_2\\ \quad\;\,|\\ CO\cdot CH_2\end{array}},$$

m. p. 170° (corr.), forms opaque crystals.

p-*Cyanophthalanilic acid*, $CN\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, crystallises in nearly colourless, silky needles; its m. p. varies with the rate of heating, but if the substance is placed in a bath at 145°, it melts at about 163°. The *anil*, $CN\cdot C_6H_4\cdot N{<}{\begin{array}{c}CO\\CO\end{array}}{>}C_6H_4$, m. p. 187° (corr.), forms feathery clusters of slender, silky needles.

When solution of formaldehyde is added to a solution of *p*-aminobenzonitrile in acetone, a condensation *product*, probably

$$CH_2(NH\cdot C_6H_4\cdot CN)_2,$$

m. p. 158°, is produced, which forms microscopic, colourless crystals.

Bromo-p-*acetylaminobenzonitrile*, $NHAc\cdot C_6H_3Br\cdot CN$, m. p. 161·5—162·5° (corr.), crystallises in colourless needles. 3-*Nitro*-4-*acetylaminobenzamide*, $NHAc\cdot C_6H_3(NO_2)\cdot CO\cdot NH_2$, m. p. 239·5° (uncorr.), obtained by the action of an alkaline solution of hydrogen peroxide on 3-nitro-4-acetylaminobenzonitrile, forms flat, yellow needles. 3:4-*Diacetylaminobenzonitrile*, $(NHAc)_2C_6H_3\cdot CN$, m. p. 238—238·5° (uncorr.), forms colourless, silky, hair-like crystals.

Cyano-α-methylbenziminazole, $CN\cdot C_6H_4{<}{\begin{array}{c}NH\\N\end{array}}{\geqslant}CMe$, m. p. 241° (uncorr.), prepared by the action of acetic acid on 3:4-diaminobenzonitrile or by the action of heat on 3:4-diacetylaminobenzonitrile, forms clusters of microscopic crystals or of opaque needles. *Carbamyl*-2-*methylbenziminazole*, $NH_2\cdot CO\cdot C_6H_3{<}{\begin{array}{c}NH\\N\end{array}}{\geqslant}CMe$, obtained by the

reduction of 3-nitro-4-acetylaminobenzonitrile with tin and acetic acid, forms colourless needles, and decomposes at about 270° (uncorr.).

E. G.

Preparation of Mercury Compounds of Sulphamidobenzoic Acid. JOHANNES KERB (D.R.-P. 242571 and 242572).—When the alkali derivatives of *o*- or *m*-sulphamidobenzoic acids are warmed in aqueous solution with one molecule of mercuric oxide (or carbonate) and the solution filtered and evaporated to dryness in a vacuum, it furnishes the *compound*, $CO_2Na \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot Hg \cdot OH$.

The second patent describes the preparation of the *compound*, $CO_2Na \cdot C_6H_3(SO_2 \cdot NH \cdot Hg \cdot OH)_2$, from 2 : 4-disulphamidobenzoic acid with mercuric oxide (2 mols.).

F. M. G. M.

New Transformations of *m*-Sulphamidobenzoic Acid under the Influence of Heat. ROKURO NAKASEKO (*Amer. Chem. J.*, 1912, **47**, 429—453).—*m*-Sulphamidobenzoic acid has m. p. 237—238°, but on prolonged heating melts at a much lower temperature. If the acid is kept in the fused state for several hours at 220—230° and is then rapidly cooled, about four-fifths of the product consists of the insoluble, amorphous modification of the acid. Another modification, m. p. 233—235°, is simultaneously produced, which is crystalline and easily soluble in water. Both these modifications were described by Limpricht and Uslar (*Annalen*, 1858, **106**, 36).

If *m*-sulphamidobenzoic acid is maintained in the fused condition for only twenty to thirty minutes and is then cooled slowly, an *ammonium hydrogen* m-*sulphobenzoate* is produced, together with another substance isomeric with *m*-sulphobenzoic diamide. The former product crystallises in hexagonal plates containing $1H_2O$, and differs in this respect from the ordinary form of ammonium hydrogen *m*-sulphobenzoate which has never been obtained with water of crystallisation. A new *barium* m-*sulphobenzoate*, $(CO_2H \cdot C_6H_4 \cdot SO_3)_2Ba,4H_2O$, is also described. The *substance* isomeric with the diamide crystallises in prisms, does not melt when heated to 253°, and is probably *m*-sulphobenzenylamidine, $SO_3H \cdot C_6H_4 \cdot C(:NH) \cdot NH_2$.

Wilson (Abstr., 1904, i, 51) has shown that *o*-sulphobenzamide can be prepared by heating potassium hydrogen *o*-sulphobenzoate with ammonium thiocyanate. Attempts to obtain *m*-sulphobenzamide in a similar manner were not successful, but resulted in the formation of two substances, one crystallising in plates and the other in needles, which were not identified.

E. G.

[Preparation of *m*-Acetylaminophenylthiolacetic and *m*-Amino-*o*-tolylthiolacetic Acids.] KALLE & Co. (D.R.-P. 244615 and 244616).—m-*Acetylaminophenylthiolacetic acid*, a yellowish-white, crystalline powder prepared by previously described methods (this vol., i, 354) from acetyl-*m*-phenylenediamine, furnishes a vat dye when treated with chlorosulphonic acid. The second patent states that m-*amino*-o-*tolylthiolacetic acid* (or its acetyl derivative), obtained from 4-acetylamino-2-toluidine in a similar manner, yields a blue vat dye when treated with condensing reagents.

F. M. G. M.

[Preparation of *s*-Xylylthiolacetic Acid.] KALLE & Co. (D.R.-P. 242997. Compare this vol., i, 126).—*m-Xylyl-5-thiolacetic acid*, needles, m. p. 85°, prepared from *m*-5-xylidine by known methods, requires a higher temperature to convert it into a dye than does the previously-described 4-carboxy-*m*-xylyl-5-thiolacetic acid.

F. M. G. M.

Unsaturated Compounds. IX. Addition of Hydroxylamine to Unsaturated Acids and Esters of the Cinnamic Acid Series and to Analogous Compounds. THEODOR POSNER (*Annalen*, 1912, 389, 1—120. Compare Abstr., 1907, i, 212).—The mechanism of additive processes and the influence of groups in the molecule of the unsaturated compound (especially those containing conjugated double linkings) and of the distribution of the affinity in the molecule of the addendum on the course of the addition are still very obscure, despite numerous researches on the subject. With the object of discovering any existent regularities in such processes, the author has examined very thoroughly the addition of hydroxylamine to cinnamic acid and its derivatives and allied substances. The influence of substituents in the nucleus, in the α- and β-positions, and in place of the acidic hydroxyl group on the additive process has been examined, but regularities have not been discovered.

It has been shown previously (Abstr., 1904, i, 160; *loc. cit.*) that, in the case of cinnamic acid itself, hydroxylamine in alcoholic solution forms a hydroxylamine salt in the cold, β-hydroxylamino-β-phenylpropionic acid after boiling for three-quarters of an hour, and β-amino-β-phenylpropionic acid after boiling for ten hours, whilst in the case of methyl or ethyl cinnamate, alcoholic hydroxylamine forms β-hydroxylaminophenylpropionic hydroxamoxime hydrate in the cold, and β-amino-β-phenylpropionic acid after prolonged boiling. In the present comparative experiments, therefore, the alcoholic hydroxylamine solution of approximately normal concentration has been used in slight excess ($2\frac{1}{2}$—3 mols. in the case of the acids, and $3\frac{1}{2}$—4 mols. in that of the esters), and the reacting mixture has been boiled for three-quarters of an hour, ten hours, or two hundred and forty hours in the case of the acids, and kept at 0° for eight days or boiled for ten hours or two hundred and forty hours in the case of the esters. Since the products of the reaction are generally easily separated from the original materials by their solubility in dilute acids, many of the experiments have been performed quantitatively. Unfortunately, this method was discovered only after the research had been in progress for some time, so that the earlier experiments are qualitative in nature, the ease of addition of hydroxylamine to cinnamic acid itself being taken as a standard of comparison. With regard to nuclear-substituted cinnamic acids and their esters, the most that can be said from the results of the experiments is that the nature and the position of the substituent have a very marked influence on the additive capacity of the C:C group of the side-chain (so far as the final product of the reactions is concerned, it will be noted that in most cases the addition of hydroxylamine has taken place at this C:C group). A certain parallelism appears to exist between the ease of addition of hydroxyl-

amine to a nuclear-substituted cinnamic acid and the dissociation constant (of the corresponding benzoic acid; data are not available for the dissociation constants of the substituted cinnamic acids). The three nitrocinnamic acids, the three methoxycinnamic acids, *m*-aminocinnamic acid, and *o*-coumaric acid do not react with hydroxylamine after boiling for three-quarters of an hour; the dissociation constants of the corresponding benzoic acids are all greater than that of benzoic acid itself. *m*- and *p*-Hydroxycinnamic acids react with hydroxylamine as easily as cinnamic acid; the dissociation constants of the corresponding benzoic acids are about the same. The ester of a nuclear-substituted cinnamic acid reacts with hydroxylamine, sometimes more readily, in other cases less so, than the acid itself.

Regularities have not been observed in the addition of hydroxylamine to α- or β-substituted cinnamic acids or their esters. The most interesting result in the case of the α-substituted acids is that the chemical nature, not the molecular weight, of the substituent appears to influence the addition of hydroxylamine; when the substituent is an alkyl or aryl group, the order with regard to increasing hindering effect is ethyl, phenyl, methyl. α-Substituted cinnamic acids and their esters unite with hydroxylamine decidedly less readily than do cinnamic acid and its esters; α-benzoylcinnamic acid and its esters, however, react as readily as cinnamic acid and its esters. β-Substituted cinnamic acids show still smaller tendency to react with hydroxylamine; with alkyl or aryl substituents the influence appears to be steric, the order of increasing hindrance being methyl, ethyl, phenyl.

So far as the final product in each case is concerned, the results of all the experiments may be summed up as follows: $\alpha\beta$-Unsaturated acids and their esters, anhydrides, amides, hydroxamic acids, and ω-nitrostyrene add the constituents of hydroxylamine at the C⁚C group; cinnamaldehyde and cinnamonitrile add on hydroxylamine at the CO or CN group, not at all or only with very great difficulty at the C⁚C group; unsaturated hydrocarbons, $\beta\gamma$-unsaturated acids, unsaturated alcohols, and ω-halogenostyrenes do not form additive compounds with hydroxylamine.

The experimental results, although not fulfilling the author's expectations, have led to several interesting discoveries. One of these is a general method for the preparation of β-aminocarboxylic acids; another is an apparently general method of obtaining aryl methyl ketones. By prolonged boiling of a cinnamic acid (except *o*- or *p*-aminocinnamic acids) with alcoholic hydroxylamine, the initially formed β-hydroxylamino-derivative is partly reduced to the β-amino-acid and partly oxidised to an oximino-compound, which may either condense to an *iso*oxazolone derivative or yield an arylmethylketoxime by loss of carbon dioxide: thus $CHAr{:}CH{\cdot}CO_2H + NH_2{\cdot}OH \longrightarrow$

$$OH{\cdot}NH{\cdot}CHAr{\cdot}CH_2{\cdot}CO_2H \longrightarrow NH_2{\cdot}CHAr{\cdot}CH_2{\cdot}CO_2H$$

and $NOH{:}CAr{\cdot}CH_2{\cdot}CO_2H \longrightarrow CArMe{:}NOH$ or $O{<}\begin{matrix}N{=}CAr \\ CO{\cdot}CH_2\end{matrix}$. The β-amino-acids are most conveniently obtained by starting with the esters of the cinnamic acids, and the aryl methyl ketones by starting with the acids themselves.

The following experimental results are recorded. The numbers after the names of the acids denote the duration in hours of the boiling with alcoholic hydroxylamine. *o*-Nitrocinnamic acid (240) yields o-*nitro-β-amino-β-phenylpropionic acid*, m. p. 222° (decomp.). Ethyl *o*-nitrocinnamate (two days at 0°) yields o-*nitro-β-hydroxylamino-β-phenylpropionhydroxamic acid*,

$$NO_2\cdot C_6H_4\cdot CH(NH\cdot OH)\cdot CH_2\cdot C(OH){:}NOH,$$

m. p. 135°, and (ten hours) *o*-nitro-*β*-amino-*β*-phenylpropionic acid. *m*-Nitrocinnamic acid yields ($\frac{3}{4}$) *hydroxylamine* m-*nitrocinnamate*, m. p. 150° (decomp.), and (10) m-*nitro-β-amino-β-phenylpropionate*, m. p. 236° (decomp.), yellow needles. Ethyl *m*-nitrocinnamate yields (four days at 0°) m-*nitro-β-hydroxylamino-β-phenylpropionhydroxamic acid*, m. p. 163—164° (decomp.), and (ten hours) *m*-nitro-*β*-amino-*β*-phenylpropionic acid. *p*-Nitrocinnamic acid (240) yields p-*nitro-β-amino-β-phenylpropionic acid*, m. p. 226° (decomp.), and p-*nitroacetophenoneoxime*, m. p. 172—173°. Ethyl *p*-nitrocinnamate (shaken for one hundred and ten hours) yields p-*nitro-β-hydroxylamino-β-phenylpropionhydroxamic acid*, m. p. 140° (decomp.), and (ten hours) *p*-nitro-*β*-amino-*β*-phenylpropionic acid. *o*-Aminocinnamic acid ($\frac{3}{4}$ or 10) and its ethyl ester, (thirty days' keeping or ten hours' boiling) yield only carbostyril. *m*-Aminocinnamic acid (10) yields m-*β-diamino-β-phenylpropionic acid*, m. p. 228° (decomp.). Ethyl *m*-aminocinnamate yields (five days at 0°) m-*amino-β-hydroxylamino-β-phenylpropionhydroxamic acid*, m. p. 100—101° (decomp.), and (ten hours) *m*-*β*-diamino-*β*-phenylpropionic acid. *o*-Coumaric acid yields (3) *β*-aminodihydro-*o*-coumaric acid, which is also obtained from the ethyl ester (10). *m*-Hydroxycinnamic acid yields ($\frac{3}{4}$) *hydroxylamine β-hydroxylamino*-m-*hydroxy-β-phenylpropionhydroxamate* (?), decomp. 129—130°, and (10) *β-amino*-m-*hydroxy-β-phenylpropionic acid*, m. p. 235—236° (decomp.). Methyl *m*-hydroxycinnamate yields (10) *β-hydroxylimino-bis*-m-*hydroxy-β-phenylpropionhydroxamic acid*,

$$OH\cdot N[CH(C_6H_4\cdot OH)\cdot CH_2\cdot C(OH){:}NOH]_2,$$

m. p. 187—188° (decomp.), and (24) *β*-amino-*m*-hydroxy-*β*-phenylpropionic acid. *p*-Hydroxycinnamic acid yields ($\frac{3}{4}$) *β-hydroxylamino*-p-*hydroxy-β-phenylpropionic acid*, m. p. 166° (decomp.), and (10) *β-amino*-p-*hydroxy-β-phenylpropionic acid*, m. p. 198° (decomp.), which is also obtained from the methyl ester (10). *cis-o*-Methoxycinnamic acid ($\frac{3}{4}$) yields *trans-o*-methoxycinnamic acid and *β-amino*-o-*methoxy-β-phenylpropionic acid*, m. p. 209—210° (decomp.) [*benzoyl* derivative, $OMe\cdot C_6H_4\cdot CH(NHBz)\cdot CH_2\cdot CO_2H$, m. p. 201°], which is also obtained from methyl *cis-o*-methoxycinnamate (10), *trans-o*-methoxycinnamic acid (10), and its methyl ester (10). *m*-Methoxycinnamic acid (10) yields *β-amino*-m-*methoxy-β-phenylpropionic acid*, m. p. 216° (decomp.), which is also obtained from the methyl ester (10). *p*-Methoxycinnamic acid (10) yields *β-amino*-p-*methoxy-β-phenylpropionic acid*, m. p. 243° (decomp.). Methyl *p*-methoxycinnamate yields (three days at 0°) *β-hydroxylamino*-p-*methoxy-β-phenylpropionhydroxamoxime hydrate*,

$$OMe\cdot C_6H_4\cdot CH(NH\cdot OH)\cdot CH_2\cdot C(NH\cdot OH)_2\cdot OH,$$

decomp. 125—129°, and (10) *β*-amino-*p*-methoxy-*β*-phenylpropionic acid. Caffeic acid (15) yields *β-aminodihydrocaffeic acid*, m. p. 196°

(decomp.). Ferulic acid (240) and its methyl ester (10) each yield *β-aminodihydroferulic acid*, m. p. 182° (decomp.). Piperonylacrylic acid (15) yields *β-aminopiperonylpropionic acid*, m. p. 233° (decomp.), and *acetopiperoneoxime*, $CH_2O_2{:}C_6H_3{\cdot}CMe{:}NOH$, m. p. 156—157°, by the hydrolysis of which acetopiperone is obtained most conveniently. Methyl piperonylacrylate (15) yields only β-aminopiperonylpropionic acid, which is converted into *β-carbamidopiperonylpropionic acid*, m. p 178—179° (decomp.), by boiling aqueous potassium cyanate.

In part, with AUGUST STIRNUS.]—α-Methylcinnamic acid (100) yields *β-amino-β-phenyl*iso*butyric acid*, $NH_2{\cdot}CHPh{\cdot}CHMe{\cdot}CO_2H$, m. p. 243° (decomp.), which is also obtained from the methyl ester (90). β-Amino-β-phenyl*iso*butyric acid forms a *hydrochloride*,

$$C_{10}H_{13}O_2N,HCl,$$

m. p. 227° (decomp.), and a *benzoyl* derivative, m. p. 205°, reacts with boiling aqueous potassium cyanate to form *β-carbamido-β-phenyl*iso*butyric acid*, m. p. 153° (decomp.) (which yields 4-*phenyl-5-methyldihydrouracil*, $CHPh{<}{\substack{CHMe{\cdot}CO\\NH\text{——}CO}}{>}NH$, m. p. 185°, at 160°), and by treatment with boiling dilute hydrochloric acid and potassium thiocyanate yields, after evaporation of the solution and heating the residue at 140°, 4-*phenyl-5-methyldihydro-3-thiouracil*,

$$CHPh{<}{\substack{CHMe{\cdot}CO\\NH\text{——}CS}}{>}NH,$$

m. p. 186°. The presence of the amino-group in the β-position in β-amino-β-phenyl*iso*butyric acid, which is proved by the formation of the preceding uracil derivatives, is confirmed by the behaviour of the acid towards nitrous acid, whereby β-hydroxy-β-phenyl*iso*butyric acid is formed.

β-Methylcinnamic acid (240) yields *β-amino-β-phenylbutyric acid*, $NH_2{\cdot}CPhMe{\cdot}CH_2{\cdot}CO_2H$, m. p. 225° (decomp.), which is also obtained from the methyl ester (10) or the ethyl ester (240), and is converted into 4-*phenyl-4-methyldihydrouracil*, m. p. 240—241°, by treatment with boiling aqueous potassium cyanate and acidifying. α-Ethylcinnamic acid yields ($\frac{3}{4}$) hydroxylamine α-ethylcinnamate and (10) *β-amino-β-phenyl-α-ethylpropionic acid*, m. p. 227° (decomp.). Methyl α-ethylcinnamate (several days at 0°) yields *β-hydroxylamino-β-phenyl-α-ethylpropionhydroxamoxime hydrate*,

$$OH{\cdot}NH{\cdot}CHPh{\cdot}CHEt{\cdot}C(NH{\cdot}OH)_2{\cdot}OH,$$

m. p. 121° (decomp.), and after thirty-five or thirty-one hours, according to the experimental conditions, either an impure *substance*, m. p. 190—215°, or *methyl hydroxyliminobis-β-phenyl-α-ethylpropionatehydroxamic acid*,

$$CO_2Me{\cdot}CHEt{\cdot}CHPh{\cdot}N(OH){\cdot}CHPh{\cdot}CHEt{\cdot}C(OH){:}NOH,$$

m. p. 228° (decomp.), or β-amino-β-phenyl-α-ethylpropionic acid. The last substance is obtained, together with some unchanged ester, from methyl α-ethylcinnamate (190). β-Ethylcinnamic acid (240) yields *β-amino-β-phenylvaleric acid*, m. p. 217° (decomp.), which is also obtained from the methyl ester (10) or ethyl ester (240), forms a pale blue *copper* salt, $2Cu(C_{11}H_{14}O_2N)_2,C_{11}H_{15}O_2N,H_2O$, and is converted into 4-*phenyl-4-ethyldihydrouracil*, m. p. 220—221°, by boiling aqueous potassium cyanate and subsequent acidification.

α-Phenylcinnamic acid yields (2) stilbene and (240) *β-amino-αβ-diphenylpropionic acid*, m. p. 225° (decomp.) (*hydrochloride*, m. p. 228°), which is also obtained from the methyl ester (10). *β-Carbamido-αβ-diphenylpropionic acid*, $NH_2\cdot CO\cdot NH\cdot CHPh\cdot CHPh\cdot CO_2H$, m. p. 141° (decomp.), is converted at 145—150° into 4 : 5-*diphenyldihydrouracil*, m. p. 268°.

β-Phenylcinnamic acid (240) yields *β-amino-ββ-diphenylpropionic acid*, m. p. 208° (decomp.). Methyl β-phenylcinnamate yields (10) 3 : 3-*diphenylisooxazolidone*, $O\lt\begin{matrix}CO-CH_2\\ NH\cdot CPh_2\end{matrix}$, m. p. 199—199·5°, and (240) a mixture of diphenyl*iso*oxazolidone and β-amino-ββ-diphenylpropionic acid. α-Benzoylaminocinnamic acid yields ($\frac{3}{4}$) *β-hydroxylamino-α-benzoylamino-β-phenylpropionic acid*,

$$OH\cdot NH\cdot CHPh\cdot CH(NHBz)\cdot CO_2H,$$

m. p. 195° (decomp.). Ethyl α-benzoylaminocinnamate (two days at 0°) yields *β-hydroxylamino-α-benzoylamino-β-phenylpropionhydroxamic acid*, $OH\cdot NH\cdot CHPh\cdot CH(NHBz)\cdot C(OH){:}NOH$, m. p. 128° (decomp.). This hydroxamic acid is converted by boiling water into *β-amino-α-benzoylamino-β-phenylpropionic acid*, m. p. 193°(decomp.), from which *β-carbamido-α-benzoylamino-β-phenylpropionic acid*, m. p. 205°, is obtained by boiling aqueous potassium cyanate.

Furylacrylic acid (288) yields a substance, m. p. 102·5°, which appears to be Bouveault's acetylfuranoxime. Methyl furylacrylate (many days at the ordinary temperature) yields *β-hydroxylamino-β-furylpropionhydroxamoxime hydrate*,

$$C_4OH_3\cdot CH(NH\cdot OH)\cdot CH_2\cdot C(NH\cdot OH)_2\cdot OH,$$

m. p. 109°. This substance, which is also obtained from ethyl furylacrylate (6), is converted by boiling water into *β-amino-β-furylpropionic acid*, m. p. 205° (decomp.) (*benzoyl* derivative, m. p. 180°). *β-Carbamido-β-furylpropionic acid* and 4-*α-furyldihydrouracil* have m. p. 175° and 210° respectively; the latter is obtained from the former at about 180°.

Atropic acid (1) yields β-amino-α-phenylpropionic acid, not α-amino-α-phenylpropionic acid as stated previously (Abstr., 1904, i, 160; 1905, i, 577); the β-amino-α-phenylpropionic acid (β-aminohydratropic acid) of the literature is really α-phenyl-β-lactamide. Phenyl*iso*crotonic acid (five minutes) yields *hydroxylamine phenyl*isocrotonate, not γ-hydroxylamino-γ-phenylbutyric acid (Abstr., 1904, i, 160).

[With Otto Unverdorben.]—Styrene, stilbene, ω-bromostyrene, ω-chlorostyrene, allyl alcohol, and amylene do not form additive compounds with hydroxylamine. ω-Nitrostyrene (many days at 0° or boiling for one hour) yields *α-nitro-β-hydroxylamino-β-phenylethane*, $NO_2\cdot CH_2\cdot CHPh\cdot NH\cdot OH$, m. p. 99—100°, colourless crystals.

Cinnamic anhydride yields ($\frac{3}{4}$) β-hydroxylamino-β-phenylpropionhydroxamoxime hydrate, or, by longer boiling, β-amino-β-phenylpropionic acid. The same results are obtained with cinnamamide and with cinnamhydroxamic acid. Cinnamonitrile (three days at 0°, or boiling for five hours) yields cinnamamideoxime.

[With Karl Rohde.]—Cinnamaldehyde yields (at 0°, or by boiling for twenty hours) cinnamaldoxime and (200) a *substance*, m. p. 205—206°, which does not contain nitrogen.

Only towards the end of the research was the discovery made that methylarylketoximes are frequently obtained by the reaction of hydroxylamine with cinnamic acids. A further communication on the subject is promised.

Other investigators have shown that ammonia, hydrogen cyanide, ethyl malonate, or ethyl acetoacetate can be added at a carbonyl group, but not at a C:C group, and, conversely, that halogens or halogen acids can be attached to a C:C group, but not to the carbonyl group. When both groups are present in the form C:C·CO, all addenda are apparently attached at the C:C group in such a manner that, if the addendum is a substance containing hydrogen and another atom or group, the hydrogen is attached in the α-, and the other constituent of the addendum in the β-, position. The author is of opinion, however, that an addendum (consisting of strongly positive hydrogen or alkali metal and another atom or group of less highly pronounced polar character, such as NH_2, NH·OH, CN, etc.) is attached at a double linking or to a conjugated system, only when the terminal atom is oxygen or nitrogen. The CO or the CN group, alone or conjugated with C:C, is able to combine with such addenda; the C:C group, alone or in conjugation with another C:C, is unable to do so. This leads to the theory that the necessary condition for the attachment of such addenda to an unsaturated system, whather simple or conjugated, is the presence in the unsaturated system of a terminal oxygen or nitrogen atom, which is the first point of attack during the addition. For example, $CHPh{:}CH{\cdot}CO_2H + NH_2{\cdot}OH \longrightarrow$

$$OH{\cdot}NH{\cdot}CHPh{\cdot}CH{:}C(OH)_2 \longrightarrow OH{\cdot}NH{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H.$$

The influence, on the course of the addition, of addenda containing like or unlike atoms of strongly polar character is discussed, and generalisations are stated which serve to account for many instances of abnormal addition. C. S.

Menthyl Esters of α-Phenyldihydrocinnamic [$\alpha\beta$-Diphenylpropionic] Acids. HANS RUPE and W. KERKOVIUS (*Ber.*, 1912, 45, 1398—1403).—*r*-$\alpha\beta$-Diphenylpropionic acid, like *r*-β-phenylbutyric acid (Abstr., 1909, i, 927), is resolved into its active constituents by esterification with menthol. The mixture of esters, obtained by the action of the alcohol on the acid chloride in the presence of pyridine and benzene, is separated by alcohol into the more fusible and more soluble menthyl *l*-$\alpha\beta$-diphenylpropionate, m. p. 58—62°, $[\alpha]_D^{20}$ $-84{\cdot}99°$ (*loc. cit.*), and the less fusible and less soluble *menthyl* d-*$\alpha\beta$-diphenylpropionate*, m. p. 100—101°, $[\alpha]_D^{20}$ $-21{\cdot}97°$. The same two esters are produced by resolving *r*-$\alpha\beta$-diphenylpropionic acid by means of its strychnine salt and esterifying the active acid chlorides.

The hydrolysis of the esters by alcoholic potassium hydroxide is accompanied by extremely rapid racemisation, since the resulting acids are optically inactive. C. S.

Preparation of Esters of Salicylic Acid. ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 244208).—*Allyl salicylate*, a colourless liquid with a cabbage-like odour, b. p.

247—250° or 105—106°/5 mm., D^{15} 1·100, is prepared by either heating salicylic acid with allyl alcohol in the presence of a condensing agent, or by the action of allyl iodide on potassium salicylate in allyl alcoholic solution. F. M. G. M.

[Preparation of Triphenylmethane Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 243086).—A description of the preparation of dyes obtained by condensing *oo'*-methylenedioxydibenzoic acids in concentrated sulphuric acid solution with derivatives of salicylic acid in the presence of an oxidising agent.

The tinctorial properties of the following condensation *products* are tabulated in the original.

s-Xylenol-2-carboxylic acid with (1) 2 : 2'-methylenedioxy-di-*m*-toluic acid, with (2) 2 : 4'-methylenedioxy-di-*m*-toluic acid, (3) with 2 : 2'-methylenedioxydibenzoic acid; and of 2 : 2'-methylenedioxy-di-*m*-toluic acid with (1) 3-hydroxy-*p*-toluic acid, with (2) *m*-chlorosalicylic acid, and with (3) 6-chloro-2-hydroxy-*m*-toluic acid.

F. M. G. M.

Homogentisic Acid. I. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1912, **78**, 306—326. Compare Abstr., 1911, i, 56).—*Benzoquinone-2-acetic acid*, $C_6H_3O_2\cdot CH_2\cdot CO_2H$, prepared by oxidation of homogentisic acid with sodium dichromate and sulphuric acid, crystallises in thin rhombohedric or quadratic plates having the same colour as lead iodide, m. p. 130° (decomp.). It tastes and reacts acid, and has the oxidising action of quinones. The clear reddish-yellow aqueous solution becomes darker when kept, and finally deposits a black sediment, characterised as homogentisic acid. On addition, first of potassium iodide and then cautiously of sodium hydroxide, a cherry-red colour is formed, which beomes olive-green on further addition of sodium hydroxide.

Homogentisic acid quinhydrone, prepared by the interaction of homogentisic acid and benzoquinoneacetic acid in acetone, forms a dark bluish-violet powder (decomp. 144°).

Benzoquinoneacetic acid also results when homogentisic acid is oxidised with ferric chloride. E. F. A.

Derivatives of 5-Nitroeugenol and of Nitrated Methoxybenzoic Acids. ALFONS KLEMENC (*Monatsh.*, 1912, **33**, 375—392). —The work is in continuation of that by Wegscheider and Klemenc (Abstr., 1911, i, 541).

Fuming nitric acid was added to a solution of eugenol in ether, the solution boiled, and the crude potassium salt of 5-nitroeugenol precipitated by addition of methyl-alcoholic potassium hydroxide. This salt was dissolved in water, and the solution treated with carbon dioxide, which precipitated 5-nitroeugenol together with a small quantity of an *acid potassium* salt of 5-nitroeugenol. Separation of these substances was effected by means of ether. The acid potassium salt of 5-nitroeugenol, $C_{20}H_{21}O_8N_2K$, is a red, crystalline substance, which decomposes at 215°. Concentrated hydrochloric acid very

slowly transforms it into 5-nitroeugenol. When boiled with water it is decomposed, and, on cooling, 5-nitroeugenol separates. Boiling alcohol (96%) also decomposes it with separation of the normal potassium salt of 5-nitroeugenol. It can also be obtained by adding 5-nitroeugenol to an aqueous solution of the normal potassium salt of 5-nitroeugenol. Methylation and subsequent oxidation of the oil so formed yields 5-nitroveratric acid.

5-Nitroeugenol methyl ether can be obtained by methylation of the normal potassium salt of 5-nitroeugenol by methyl iodide, or, better, by treating an ethereal solution of 5-nitroeugenol with diazomethane. Methylation by means of methyl sulphate is difficult. Oxidation of 5-nitroeugenol methyl ether in dilute acetic acid solution by means of potassium permanganate gives a mixture of 5-nitroveratric acid and 5-nitrohomoveratric acid. Oxidation in alkaline solution yields 5-nitroveratric acid.

5-*Nitrohomovanillic acid*, m. p. 217° (decomp.), was obtained by the oxidation of 5-nitroacetyleugenol by means of potassium permanganate in very dilute acetic acid solution. Its *ammonium* and *silver* salts were examined. The crude oxidation product generally contains also 5-nitrovanillic acid. If smaller quantities of water are employed, the yield of 5-nitrohomovanillic acid is less, whilst if the oxidation is performed in glacial acetic acid solution, still less 5-nitrohomovanillic acid and more 5-nitrovanillic acid is produced.

Methyl 5-*nitrohomovanillate*, m. p. 101—102°, was transformed into its *potassium* salt, and the latter boiled with methyl iodide in methyl alcoholic solution. The crude oil was cautiously saponified by potassium hydroxide, and the liberated acids recrystallised from benzene, whereby 5-*nitrohomoveratric acid*, m. p. 113—114°, was obtained. Its *ammonium*, *silver*, *uranyl*, and *copper* salts were examined. The methylation of 5-nitrohomovanillic acid is more readily accomplished by means of diazomethane. Methyl sulphate is without action on the acid or its ester.

5-Nitroveratric acid was boiled with aniline during thirty minutes, whereby it was transformed into 5-nitrovanillic acid and 6-nitroguaiacol. More prolonged boiling increased the yield of 6-nitroguaiacol at the expense of the 5-nitrovanillic acid, a black mass, insoluble in alkali, being simultaneously formed. 5-Nitroveratric acid was stable towards boiling concentrated hydrochloric acid. Boiling concentrated potassium hydroxide caused slow elimination of a methoxy-group.

Methyl 5-*nitrovanillate* forms yellow needles, m. p. 154—155°.

5-Nitroveratric acid, when treated with cold fuming nitric acid (D 1·52), yields 3 : 4 : 5-trinitroveratrole and 5 : 6-*dinitroveratric acid*, m. p. 193°. This acid is also obtained by cautious saponification of its *methyl* ester. Its *ferric*, *ammonium*, and *copper* salts were examined. When the ammonium salt is heated at 180—200°, methyl 5 : 6-dinitroveratrate, m. p. 133—134°, is obtained. Distillation of a mixture of the *potassium* salt and lime leads to the formation of methyl 5 : 6-dintroveratrate and 5 : 6-*dinitrovanillic acid*, m. p. 215° (decomp.). Nitration of methyl 5-nitroveratrate by means of fuming nitric acid (D 1·52) at 60° gives an almost quantitative yield of methyl

5:6-dinitroveratrate, m. p. 133—134·5°. This, when saponified by boiling potassium hydroxide, yields 5:6-dinitrovanillic acid, the *ferric* salt of which was examined. The acid could not be acetylated by acetic anhydride and sulphuric acid. H. W.

The Coumarin Group. EINAR BIILMANN (*Annalen*, 1912, **388**, 259—279).—Despite numerous researches on coumarin and its derivatives, satisfactory explanations have not yet been given of the slight activity of its ethylenic linking and of the conversion of coumarin into coumaric acid. In connexion with the first problem, the author utilises the fact that ethylene derivatives containing two negative groups do or do not form complex mercuri-compounds according as the two groups have the *cis-* or the *trans*-configuration (Abstr., 1902, i, 665; 1910, i, 346). Methylcoumarinic acid reacts with mercuric acetate in methyl alcohol to form an *inner* salt of *a-mercuri-β-methoxy-β-*o*-anisylpropionic acid*,

$$OMe\cdot C_6H_4\cdot CH(OMe)\cdot CH<\begin{matrix}Hg\\ |\\ CO_2\end{matrix},$$

a white, microcrystalline substance which is converted into *β-methoxy-β-*o*-anisylpropionic acid*, m. p. 82°, by hydrogen sulphide in alkaline solution. Coumarin does not react with methyl alcoholic mercuric acetate, a fact which, taken in conjunction with the unstable character of the additive compounds of coumarin and bromine and hydrogen bromide (Clayton, Trans., 1908, **93**, 524), indicates that coumarin does not contain an ordinary ethylenic linking.

[With ULLA. STARCKE.]—Contrary to expectation, coumaric acid and methylcoumaric acid each react with mercuric acetate in methyl alcohol. The former yields the *inner* salt of *a-mercuri-β-methoxymelilotic acid*, $OH\cdot C_6H_4\cdot CH(OMe)\cdot CH<\begin{matrix}Hg\\ |\\ CO_2\end{matrix}$, which is converted into *β-methoxymelilotic acid*, $OH\cdot C_6H_4\cdot CH(OMe)\cdot CH_2\cdot CO_2H$, m. p. 123° (decomp.), by hydrogen sulphide in alkaline solution. Methylcoumaric acid yields an *inner* salt isomeric with that obtained from methylcoumarinic acid; it is converted into the same acid, m. p. 82°, by hydrogen sulphide.

[With AGNES HOFF.]—It is known that the conversion of coumarin into coumaric acid is effected very slowly by boiling aqueous alkali, but proceeds very rapidly when the lactone is heated with alcoholic sodium ethoxide and the solution is treated with water and acidified after removal of the alcohol; ethyl coumarate is formed as an intermediate product (Fries and Klostermann, Abstr., 1908, i, 820). The following three experiments throw light on the course of the change: (1) Coumarin dissolves in cold methyl alcoholic sodium methoxide with an intense yellow colour; acidification by dilute acetic acid regenerates coumarin. (2) Coumarin and sodium methoxide (2 mols.) are kept in methyl alcoholic solution at the ordinary temperature for a few hours. Ice-water and acetic acid are then added, whereby a mixture of coumarin, methyl coumarate, and an oil (which yields β-methoxymelilotic acid by hydrolysis, and is almost certainly its methyl ester) is obtained. (3) Same as (2) except that after the addition of the

water the mixture is kept for twelve to thirty-six hours before acidifying. A mixture of coumarin, coumaric acid, and β-methoxymelilotic acid is thus obtained.

These results are interpreted as follows: The yellow substance obtained in (1) is the additive compound, $ONa\cdot C_6H_4\cdot CH\colon CH\cdot CO_2Me$. The product of acidification is methyl coumarinate, which at once regenerates coumarin. In the presence of an excess of sodium methoxide, the additive compound takes up another molecule of methyl alcohol, and forms the sodium derivative of methyl β-methoxymelilotate, $ONa\cdot C_6H_4\cdot CH(OMe)\cdot CH_2\cdot CO_2Me$, by the acidification of which the oil (methyl β-methoxymelilotate ?) is formed. (*Methyl-β-methoxymelilotate*, obtained from the silver salt and methyl iodide, is an oil very similar to the preceding, and is converted into methyl coumarate by methyl alcoholic sodium methoxide.) By long keeping before acidification, however, the sodium derivative of methyl β-methoxymelilotate loses methyl alcohol, and forms the sodium derivative of, not methyl coumarinate, but methyl coumarate, so that coumaric acid is finally obtained by acidification and the accompanying hydrolysis.

When experiments similar to the preceding are performed with sodium methoxide and ethyl alcohol, ethyl coumarate, coumaric acid, and *β-ethoxymelilotic acid*, m. p. 98°, are obtained. C. S.

Cyanohydrins, and the Corresponding Benzoylamides and Alcohols. JULES ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1912, [iv], 11, 389—393).—The authors have applied the methods of Francis and Davis (Trans., 1909, **95**, 1403; 1910, **97**, 949) for the preparation of acyl derivatives of aldehyde-cyanohydrins to a number of phenolic aldehydes, and in some cases have prepared the corresponding benzoyl amides and hydroxy-acids.

p-Hydroxybenzaldehyde with benzoyl chloride and potassium cyanide yields p-*benzoyloxybenzoylmandelonitrile* [*a*: 4-*dibenzoyloxyphenylacetonitrile*], m. p. 143—144°, which crystallises from chloroform on addition of ether. 4-*Benzoyloxybenzoyl*-m-*tolylglycollonitrile* [*a*: 4-*dibenzoyloxy*-o-*tolylacetonitrile*], $OBz\cdot C_6H_3Me\cdot CH(OBz)\cdot CN$, m. p. 124—125°, similarly obtained from 4-hydroxy-*m*-tolualdehyde, forms colourless crystals. The corresponding *substance* obtained from vanillin has m. p. 146—147°. Salicylaldehyde gives a liquid compound. All these products are stable, and do not decompose when heated at 100° for several hours.

Benzoylmandelonitrile in contact with fuming hydrochloric acid at atmospheric temperature furnishes benzoylmandelamide. In the case of the dibenzoylcyanohydrins derived from the phenolic aldehydes it is better to heat them at 100° in closed tubes with hydrochloric acid. Under these conditions, *p*-benzoyloxybenzoylmandelonitrile furnishes the corresponding *amide*, $OBz\cdot C_6H_4\cdot CH(OBz)\cdot CO\cdot NH_2$, m. p. 183—184°, colourless crystals, soluble in alcohol, insoluble in water, which on hydrolysis by sodium hydroxide solution gives *p*-hydroxymandelic acid. It is not always necessary to isolate the amide in order to convert it into the corresponding hydroxy-acid; thus the benzoylcyanohydrin derived from anisaldehyde on long keeping

with fuming hydrochloric acid at atmospheric temperature, yields *p*-methoxymandelic acid. T. A. H.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXIV. Esterification of Amino- and Acetamino-terephthalic Acids. RUDOLF WEGSCHEIDER and FRANZ FALTIS (*Monatsh.*, 1912, 33, 185—205. Compare Cahn Speyer, Abstr., 1907, i, 849).—When the amino-group in aminoterephthalic acid is regarded as positive, the carboxyl group in position 4 is the stronger acid, and the least affected by steric hindrance. According to Wegscheider's rule, when esterified by alcohol, with or without mineral acids, or by methyl iodide, aminoterephthalic acid should give salts of the 4-ester acid, whereas on partial hydrolysis of the neutral ester, the 1-ester acid should be formed. Experiment shows that this hydrolysis gives rise likewise to the 4-ester acid, affording an exception to the rule.

In the case of acetylaminoterephthalic acid, the acetylamino-group is negative; accordingly, when esterified by methyl iodide, the 1-ester acid should result, as is actually the case. On esterification with methyl alcohol, the 4-ester acid is formed; in both cases the acetyl group is eliminated during the process. Hydrolysis of the neutral ester of acetylaminoterephthalic acid yields the 4-ester acid instead of the 1-ester acid forecasted by Wegscheider's rule.

Acetylaminoterephthalic acid has decomp. 272° (corr.); it crystallises $+CH_3OH$ from solution in methyl alcohol in large, lustrous, golden-yellow aggregates.

4-Methyl 1-hydrogen 2-acetylaminoterephthalate crystallises in colourless, stunted needles, m. p. 207—208° (corr.), becoming solid again at 245°, and finally melting at 305° (compare Cahn-Speyer, *loc. cit.*).

Methyl acetylanthranilcarboxylate, formed on prolonged heating of the 2-acetylamino-4-ester acid with a large excess of acetic anhydride, has m. p. 148—149° (corr.), becoming solid at about 265°.

E. F. A.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXV. Esterification of Dimethylaminoterephthalic Acid. RUDOLF WEGSCHEIDER and SIEGMUND BLACK (*Monatsh.*, 1912, 33, 207—221).—According to Wegscheider's rule the main product on esterification of dimethylaminoterephthalic acid with alcohols, with or without mineral acids, or by means of alkyl iodides should be the 4-ester acid, whereas on partial hydrolysis of the neutral ester the 1-ester acid should result.

This is the case when methyl-alcoholic potassium hydroxide is used for hydrolysis, but when the neutral ester is hydrolysed in neutral or acid, and probably also in alkaline, aqueous solution, the 4-ester acid predominates. This is the first time on which such a pronounced influence of the solvent on hydrolysis has been recorded.

The following salts of dimethylaminoterephthalic acid are described: *potassium hydrogen* salt $+2H_2O$, decomp. 160°; *silver hydrogen* salt, which is faintly yellow-coloured, decomp. 200°; *silver* salt, which is at first colourless, but becomes deep blue overnight and black when dried.

4-*Methyl* 1-*hydrogen* 2-*dimethylaminoterephthalate* forms colourless, slender crystals, m. p. 172—174°.

1-*Methyl* 4-*hydrogen* 2-*dimethylaminoterephthalate* crystallises in slender, golden-yellow needles, m. p. 132—133°. E. F. A.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXVI. Esterification of Methyl Aminoterephthalic Acid. RUDOLF WEGSCHEIDER and OSKAR HUPPERT (*Monatsh.*, 1912, **33**, 223—234).—Contrary to the behaviour of aminoterephthalic acid and its dimethylamino-derivative, methyl aminoterephthalic acid behaves quite normally when its neutral ester is partly hydrolysed with potassium hydroxide or hydrogen chloride in aqueous or methyl alcoholic solution, forming the 1-ester acid. By the action of methyl iodide on the normal silver or acid potassium salts, 4-methyl 1-hydrogen dimethylaminoterephthalate is obtained.

The *silver* salt of methylaminoterephthalic acid is light yellowish-brown when freshly precipitated, but quickly becomes darker.

The *potassium hydrogen* salt crystallises in lustrous, silvery plates; it is yellow after drying at 100°.

The normal ester has m. p. 89—90°; it is triclinic [$a:b:c=0{\cdot}643:1:0{\cdot}9907$]. It has a citron-yellow colour with a blue fluorescence.

1-*Methyl* 4-*hydrogen* 2-*methylaminoterephthalate* crystallises in platelets, m. p. 208·5—209·5° (corr.).

The 4-methyl ester acid of 2-dimethylaminoterephthalic acid (compare Wegscheider and Black, preceding abstract), m. p. 178—179°, forms measureable triclinic crystals [$a:b:c=0{\cdot}7908:1:0{\cdot}8297$].

E. F. A.

Action of Oxalyl Chloride on Aromatic Hydrocarbons. CARL LIEBERMANN [with M. KARDOS, W. RAHTS, PROFULLA MITTER, and D. BUTESCU] (*Ber.*, 1912, **45**, 1186—1217. Compare Abstr., 1911, i, 202, 387).—Whereas diphenyl with oxalyl chloride yields mainly monocarboxylic acid, 4 : 4′-dimethyldiphenyl with the same reagent yields mainly dicarboxylic acid with a considerable proportion of quinone (dimethylphenanthraquinone). Other 4 : 4′-derivatives have now been studied: 4 : 4′-dinitrodiphenyl does not react with oxalyl chloride and aluminium chloride; 4 : 4′-dibromodiphenyl only gives very little acid, whilst 4 : 4′-dimethoxydiphenyl gives very little monocarboxylic acid. With 3 : 3′- and 2 : 2′-dimethyldiphenyl considerable quantities of dicarboxylic acid and a little monocarboxylic acid were obtained, but no quinone.

With 2 : 4 : 2′ : 4′-dixylyl, which contains methyl groups in the para- and ortho-positions, dicarboxylic acid and no quinone was obtained.

Anthracene derivatives, substituted in the benzene nucleus, yielded in every case *meso*-anthracenemonocarboxylic acids and aceanthrene-quinones.

Phenyl radicles joined through a methane or aliphatic group give rise to acids and not quinones with oxalyl chloride. In these cases the higher carboxylic acids are formed; thus triphenylmethane yields

tri- and di-carboxylic acids. From stilbene, carboxylic acids of a polymerised stilbene were obtained.

Increase of the number of methyl groups in the benzene nucleus has no effect; the three isomeric xylenes give monocarboxylic acids.

On oxidation of 4 : 4′-dimethylphenanthraquinone with chromic acid the methyl groups are oxidised to carboxyl, and one of the latter is eliminated, so that phenanthraquinonemonocarboxylic acid is obtained, which could not be further oxidised without complete decomposition.

It was possible, however, to convert dimethylphenanthraquinone-oxime into 4 : 4′-dimethyldiphenyl-2 : 2′-dicarboxylic acid, isomeric with 4 : 4′-dimethyldiphenic acid.

These compounds are further oxidised to tetracarboxylic acids, which differ mainly in the melting points of their methyl esters, and in the fluorescein reaction with resorcinol without zinc chloride. The exact position of the groups is discussed; it has not yet been established with certainty.

Oxalyl chloride affords a very satisfactory means of introducing carboxyl groups into aromatic hydrocarbons, and when methyl groups are also present in the phenyl radicle, higher carboxylic acids are readily obtained on oxidation. Oxalyl chloride differs in its action from phosgene, which mainly yields ketones and probably acts in virtue of the complex CO·COCl.

[With M. KARDOS.]—2 : 7-*Dimethylphenanthrene*-9 : 10-*diol*,

$$C_{14}H_6Me_2(OH)_2,$$

obtained from the corresponding quinone by reduction with zinc dust and acetic acid, crystallises in well-formed, long, colourless needles in the tube, but it is soon darkened on access of air, m. p. 175—180°; the *quinhydrone* could not be obtained pure.

2 : 7-*Dimethylphenanthraquinonemono-oxime* crystallises in lustrous, silky, yellow needles, m. p. 180—181°, and dissolves in concentrated sulphuric acid with a faint violet coloration. When dissolved in acetic anhydride and heated with hydrogen chloride, it undergoes rearrangement, and 4 : 4′-*dimethyldiphenyl*-2 : 2′-*dicarboxylic* acid is obtained in microscopic platelets, m. p. 258—260°. It does not give a fluorescein reaction with resorcinol; the *methyl* ester has m. p. 91—92°.

Diphenyl-2 : 4 : 2′ : 4′-*tetracarboxylic acid*, $C_{12}H_6(CO_2H)_4$, obtained on oxidation with potassium permanganate, is not melted at 325°, and does not form an anhydride; the *tetramethyl* ester has m. p. 181—182°.

4 : 4′-*Dimethyldiphenylcarboxylic acid*, $C_{12}H_7Me_2{\cdot}CO_2H$, has m. p. 197°.

4 : 4′-Dimethyldiphenyl-2 : 3′(?)-dicarboxylic acid forms an *ethyl* ester, m. p. 66—67°, a *methyl* ester, m. p. 113—115°, and a crystalline *chloride*, $C_{12}H_6Me_2(COCl)_2$, m. p. 170—171°.

4 : 4′-*Dimethyldiphenyldicarboxylic anhydride*, prepared by heating the acid with acetic anhydride at 160—170°, crystallises in long needles, m. p. 286°.

Diphenyl 4 : 4′ : 2 : 3′(?)-*tetracarboxylic acid* has m. p. 290°, and sublimes at this temperature. When heated with acetyl chloride, it appears to form mono- and di-anhydrides. On fusion with resorcinol an orange fluorescein is obtained. The *methyl* ester has m. p. 99—100°.

3 : 3′-Dimethyldiphenyl-4 : 4′-dicarboxylic acid, obtained from 3 : 3′-dimethyldiphenyl and oxalyl chloride, has m. p. above 300° (compare Loewenherz, Abstr., 1892, 852); the *methyl* ester crystallises in lustrous, silky needles, m. p. 137°; the *ethyl* ester has m. p. 77—78°. Diphenyl-3 : 3′ : 4 : 4′-tetracarboxylic acid, obtained on oxidation, has m. p. above 300°; the *methyl* ester crystallises in transparent prisms, m. p. 99—100°. The acid (compare Loewenherz, *loc. cit.*) sublimes with difficulty in snow-like flakes; on heating at 100—115° the dianhydride is readily formed.

2 : 4 : 2′ : 4′-*Tetramethyldiphenyldicarboxylic acid*, prepared from the corresponding tetramethylphenyl and oxalyl chloride, has m. p. 320—322°. On oxidation, *diphenyl* 2 : 2′ : 4 : 4′ : 6 : 6′(?)-*hexacarboxylic acid*, $C_{12}H_4(CO_2H)_6$, is formed, m. p. above 300°; the *methyl* ester crystallises in needles, m. p. 202—204°. On oxidation of dimethylphenanthraquinone, 9 : 10-phenanthraquinone-2-carboxylic acid is obtained (compare Werner and Ney, Abstr., 1902, i, 441); this crystallises in red needles and sublimes also in red needles.

4 : 4′-*Dimethoxydiphenylcarboxylic acid*, $C_{12}H_7(OMe)_2\cdot CO_2H$, crystallises in needles, m. p. 180°.

[With W. Rahts.]—p-*Tolylphenylmethanedicarboxylic acid*,

$$CO_2H\cdot C_6H_3Me\cdot CH_2\cdot C_6H_4\cdot CO_2H,$$

crystallises in colourless plates, m. p. 337°; the *dimethyl* ester has m. p. 94°.

Di-p-*tolylmethanedicarboxylic acid* has m. p. above 300°.

2 : 2′-*Dimethyldiphenyldicarboxylic acid* forms colourless plates, m. p. 287°; the *dimethyl* ester separates in colourless needles, m. p. 124°.

The *diphenyltetracarboxylic acid* obtained on oxidation has m. p. 334°; the *tetramethyl* ester has m. p. 141°; the acid gives only very little fluorescein with resorcinol

[With Profulla Mitter.]—*Dinitro-diphenylmethane*-4 : 4′-*dicarboxylic acid* crystallises in slender needles, m. p. 271° (decomp.).

Methyl diphenylmethane-4 : 4′-*dicarboxylate* forms slender needles, m. p. 81—82°.

Dibenzyl-*p*-carboxylic acid separates in slender needles, m. p. 173—174° (not 228—230° as stated previously, Abstr., 1911, i, 202). The *sodium* salt, glistening platelets, and *calcium* salt, slender needles, are described. On oxidation, benzoic and terephthalic acids are obtained.

Dibenzyl-4 : 4′-dicarboxylic acid has m. p. 320°; the dimethyl ester crystallises in needles, m. p. 119° (compare Wolffenstein and Fischer, Abstr., 1904, i, 896).

Triphenylmethanetricarboxylic acid crystallises in prisms, m. p. 215° (decomp.).

Stilbenecarboxylic acid (?), $CHPh{:}CH\cdot C_6H_4\cdot CO_2H$, has m. p. 235—237°; the *methyl* ester is a yellow powder, m. p. 145°.

Stilbenedicarboxylic acid, $C_2H_2(C_6H_4\cdot CO_2H)_2$, has m. p. 225° (decomp.). It could not be reduced. The above acids are regarded as derivatives of polymerised stilbene. With aluminium chloride, stilbene forms a polymeride, m. p. 220°.

[With D. BUTESCU.]—*β-Methylanthracene*-10-*carboxylic acid*,

$$C_6H_4<\begin{matrix}CH\text{———}\\ \mid\\ C(CO_2H)\end{matrix}>C_6H_3Me,$$

is colourless, m. p. 197°.

β-Methylaceanthrenequinone crystallises in well-formed, red needles, m. p. 251°.

β-Chloroanthracene-10-*carboxylic acid* separates in pale yellow needles, m. p. 228°.

β-Chloraceanthrenequinone forms red needles, m. p. 294—295°.

α-Chloroanthracene-10-*carboxylic acid*,

$$C_6H_4<\begin{matrix}CH\text{———}\\ \mid\\ C(CO_2H)\end{matrix}>C_6H_3Cl,$$

crystallises in bunches of pale yellow needles, m. p. 258° (decomp.).

α-Chloroaceanthrenequinone is more soluble in benzene than the β-isomeride; it forms red needles, m. p. 251° (decomp.).

1 : 8-*Dichloroanthracene*-10-*carboxylic acid* crystallises in fan-like aggregates of yellow platelets, m. p. above 270°.

1 : 8-*Dichloroaceanthrenequinone* forms pale brown plates, m. p. 268—270° (decomp.).

1 : 5-*Dichloroanthracene*-10-*carboxylic acid* separates in pale yellow needles, m. p. 205° (decomp.).

1 : 5-*Dichloroaceanthrenequinone* forms red needles, m. p. above 275°.

E. F. A.

Synthesis of ωω-Diphenyl-1 : 4-naphthaquinomethane (*p*-Naphthafuchsone) and of Allied Compounds. ZOFJA ZALESKA-MAZURKIEWICZ and AUGUSTIN BISTRZYCKI (*Ber.*, 1912, **45**, 1429—1440. Compare Abstr., 1901, i, 701; 1904, i, 44).—Since benzilic acid condenses with α-naphthol to form, not the desired diphenyl-4-hydroxy-naphthylacetic acid, but the lactone of diphenyl-1-hydroxy-β-naphthyl-acetic acid (Geipert, Abstr., 1904, i, 318), the following device has been employed in the synthesis of *p*-naphthafuchsone. A boiling benzene solution of benzilic acid and 1-hydroxy-2-naphthoic acid is treated with anhydrous tin tetrachloride (1 mol.), whereby *diphenyl*-4-*hydroxy*-3-*carboxynaphthylacetic acid*, $CO_2H\cdot C_{10}H_5(OH)\cdot CPh_2\cdot CO_2H$, m. p. 237—240° (decomp.), is obtained. *Diphenyl*-4-*hydroxy*-3-*carbomethoxynaphthylacetic acid*, m. p. 229° (decomp.), is prepared in a similar manner from methyl 1-hydroxy-2-naphthoate. The *dimethyl* ester has m. p. 211—212°.

A solution of diphenyl-4-hydroxy-3-carboxynaphthylacetic acid in concentrated sulphuric acid evolves carbon monoxide at 50—60°, whereby is formed *diphenyl*-4-*hydroxy*-3-*carboxynaphthylcarbinol*,

$$CO_2H\cdot C_{10}H_5(OH)\cdot CPh_2\cdot OH,$$

which crystallises in yellow prisms, darkens at about 135° and decomposes at 196—198°, and is converted by zinc dust and boiling 95% acetic acid into *diphenyl*-4-*hydroxy*-3-*carboxynaphthylmethane*,

$$CO_2H\cdot C_{10}H_5(OH)\cdot CHPh_2,$$

decomp. 207°. Diphenyl-4-hydroxy-3-carboxynaphthylcarbinol is converted by boiling *N*-potassium hydroxide or by *N*/2-potassium hydroxide at 140—145° into *ωω-diphenyl*-1 : 4-*naphthaquinomethane*,

(p-*naphthafuchsone*), $O:C_{10}H_6:CPh_2$, m. p. 179°, yellow needles, which develops a deep violet coloration with concentrated sulphuric acid, is remarkably stable to hot aqueous or alcoholic potassium hydroxide, and is reduced to diphenyl-4-hydroxynaphthylmethane by boiling 95% acetic acid and zinc dust.

Compounds analogous to the preceding have been obtained from *pp'*-tolilic acid and 1-hydroxy-2-naphthoic acid. *Di*-p-*tolyl*-4-*hydroxy*-3-*carboxynaphthylacetic acid* crystallises from diluted alcohol in colourless plates containing EtOH, decomp. 205—216°, and forms a *dimethyl* ester, m. p. 233° (decomp.). *Di*-p-*tolyl*-4-*hydroxy*-3-*carboxynaphthylcarbinol*, $C_{26}H_{22}O_4,H_2O$, almost colourless needles, has m. p. 116° (decomp.). *ωω-Di*-p-*tolyl*-1 : 4-*naphthaquinomethane*, yellow needles, has m. p. 165°.

The condensation of diphenyleneglycollic acid and 1-hydroxy-2-naphthoic acid in boiling benzene in the presence of tin tetrachloride yields *diphenylyl*-4-*hydroxy*-3-*carboxynaphthylacetic acid*,

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>C(CO_2H)\cdot C_{10}H_5(OH)\cdot CO_2H,$$

m. p. 213—223° (decomp.), which dissolves in warm concentrated sulphuric acid with a deep green colour, but does not thereby yield the expected carbinolcarboxylic acid C. S.

[Preparation of Anthraquinone Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 243750. Compare Abstr., 1911, i, 980).—1-Arylthiolanthraquinone-2-carboxylic acids are readily prepared by the action of aryl mercaptans on 1-halogen- or 1-nitroanthraquinone-2-carboxylic acids in the presence of a condensing agent.

1-p-*Tolylthiolanthraquinone*-2-*carboxylic acid*, a yellow powder, is thus obtained from *p*-thiocresol and 1-chloroanthraquinone-2-carboxylic acid; when treated with phosphorus pentachloride, it furnishes a *thioxanthone*, dark red needles.

1-p-*Chlorophenylthiolanthraquinone*-2-*carboxylic acid* is yellow, and the corresponding thioxanthone an orange-yellow powder.

1-*β*-*Naphthylthiolanthraquinone*-2-*carboxylic acid*, an orange-red powder, yields an orange-brown powder when treated with phosphorus pentachloride.

1-*β*-*Anthraquinonylthiolanthraquinone*-2-*carboxylic acid*, an orange powder, is prepared from *β*-mercaptoanthraquinone and 1-chloroanthraquinone-2-carboxylic acid, it furnishes a brownish-yellow powder with phosphorus pentachloride. F. M. G. M.

Tannin. IX. MAXIMILIAN NIERENSTEIN (*Annalen*, 1912, **388**, 223—258. Compare Abstr., 1911, i, 642).—The author has abandoned the use of the names "tannin" for digallic acid and "leucotannin" for leucodigallic acid; he now uses the name "tannin" to denote the polydigalloyl-leucodigallic anhydrides mentioned below.

Leucodigallic acid, $C_6H_2(OH)_3\cdot CH(OH)\cdot O\cdot C_6H_2(OH)_2\cdot CO_2H$, previously only known in the form of its penta- and hexa-acetyl derivatives, has been obtained as a mixture of the *d*- and of the *dl*-forms by boiling an aqueous solution of tannin (*tanninum levissimum purissimum*, Schering) with zinc dust according to Iljin's method

(Abstr., 1910, i, 331), gallic acid and gallaldehyde also being formed in the reaction. *dl*-Leucodigallic acid has also been obtained by the reduction of digallic acid by zinc dust and water, alcohol, or acetic acid, and by calcium hydride and moist ether; it has m. p. 278—280°, crystallises in fine needles, and does not exhibit tannoid properties (that is, is not absorbed by casein or precipitated by gelatin). The penta-acetyl derivative obtained directly from the acid and boiling acetic anhydride has m. p. 172—173°. *Hexaethylcarbonatoleucodigallic acid*, $C_6H_2(O\cdot CO_2Et)_3\cdot CH(O\cdot CO_2Et)\cdot O\cdot C_6H_2(O\cdot CO_2Et)_2\cdot CO_2H$, has m. p. 123° (decomp.).

The resolution of *dl*-leucodigallic acid itself cannot be effected. An alcoholic solution of *dl*-hexaethylcarbonatoleucodigallic acid, however, is readily resolved by strychnine. l-*Hexaethylcarbonatoleucodigallic acid*, small needles, has m. p. 127—128° (decomp.), and $[\alpha]_D^{15} - 57\cdot35°$ in alcohol. d-*Hexaethylcarbonatoleucodigallic acid*, small scales, has m. p. 132—134° (decomp.), and $[\alpha]_D^{18} + 62\cdot50°$. These two derivatives are converted into their active parent acids by warming with 1% pyridine. l-*Leucodigallic acid*, m. p. 276—277° (decomp.), crystallises in needles, does not exhibit tannoid properties, and has $[\alpha]_D^{15} - 70\cdot26°$ in water, diminishing to $-64\cdot58°$ after ten days. d-*Leucodigallic acid*, m. p. 276—277°, $[\alpha]_D^{19} + 104\cdot2°$ in water, $[\alpha]_D^{17} + 56\cdot4°$, in alcohol, crystallises in stellate clusters of needles; d-*penta-acetyl-leucodigallic acid*, obtained by resolving the *dl*-form by strychnine, has m. p. 171° and $[\alpha]_D^{18} + 76\cdot4°$ in acetone.

Leucodigallic acid yields gallaldehyde and gallic acid by hydrolysis with dilute sulphuric acid, is oxidised to ellagic acid and luteo-acid (pentahydroxydiphenylmethylolidecarboxylic acid) by 10% hydrogen peroxide in boiling aqueous solution, and is converted into purpurotannin by potassium persulphate and sulphuric acid in glacial acetic acid. Penta- and hexa-acetyl-leucodigallic acids are not attacked by benzoyl chloride and potassium cyanide in a similar manner to penta-acetyldigallic acid (Abstr., 1911, i, 642). As regards the nature of their condensation products with formaldehyde in the presence of hydrochloric acid, leucodigallic acid resembles tannin in yielding more than 90% of hydroxyaurincarboxylic acids soluble in water and very little diphenylmethane derivatives insoluble in water, whilst digallic acid resembles gallic acid in yielding 15 to 20% of the first type and about 80% of the second type of condensation products (compare Nierenstein and Webster, Abstr., 1908, i, 89).

From the results of his earlier researches, the author has previously regarded tannin as a mixture of digallic and leucodigallic acids containing a little gallic acid. The fact, however, that leucodigallic acid does not exhibit tannoid properties, whilst tannin is absorbed almost quantitatively by casein, prove that free leucodigallic acid cannot be a constituent of tannin. Further arguments against the view that tannin is a mixture of the three acids mentioned above are (1) the high molecular weight of tannin; (2) tannin scarcely conducts electrolytically, whereas digallic acid does so well (Herzig and Renner, Abstr., 1909, i, 713); (3) the methoxy value of methylotannin corresponds with four hydroxyl groups, not with five as in the case of digallic acid, or six as in the case of leucodigallic acids (Herzig, Abstr, 1905, i, 354).

Hence for these reasons, and from the fact that the acetylation of tannin by acetic anhydride yields a product containing 18·49 to 22·71% of penta-acetyl-leucodigallic acid, the author withdraws his former opinion of the constitution of tannin, and ascribes to tannins the compositions of polydigalloyl-leucodigallic anhydrides,

$$OH\cdot[C_6H_2(OH)_2\cdot CO\cdot O]_x\cdot C_6H_2(OH)<\begin{matrix}O\cdot CO\cdot C_6H_2(OH)_2\cdot O\\ CO\cdot O\cdot C_6H_2(OH)_2\cdot CH\cdot OH\end{matrix},$$

corresponding with those of Fischer and Freudenberg's depsides (Abstr., 1910, i, 265). According to this view, the simplest tannin would be digalloyl-leucodigallic anhydride,

$$C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(OH)<\begin{matrix}O\cdot CO\cdot C_6H_2(OH)_2\cdot O\\ CO\cdot O\cdot C_6H_2(OH)_2\cdot CH\cdot OH\end{matrix}.$$

Since, however, the tannin used by the author (*tanninum levissimmn purissimum*, Schering) yields digallic and leucodigallic acids in the proportions 3 : 1 and 4 : 1, such tannin must be tri- or tetra-digalloyl-leucodigallic anhydride. The author shows that this constitution of his tannin meets satisfactorily the above-mentioned objections to his former view of its constitution.

Tannin in pyridine cooled by a freezing mixture yields, by treatment with acetyl chloride, a little triacetylgallic acid and a white, amorphous *substance*, m. p. 218—224° (decomp.), which does not give a coloration with ferric chloride, forms a *sodium* salt with 10% sodium carbonate in the cold, and from its analysis, basicity, and percentage of acetyl is *octadecylacetyltridigalloyl-leucodigallic acid*, $C_{91}H_{71}O_{49}\cdot CO_2H$. This constitution is supported by the fact that the reaction of the substance with ethyl chlorocarbonate and aqueous potassium cyanide in a freezing mixture yields triacetylgalloyl cyanide, ethylcarbonatodiacetylgalloyl cyanide (both identified, after hydrolysis, as galloylformic acid), and d-*ethylcarbonatopenta-acetyl-leucodigallic acid*,

$$C_6H_2(OCO_2Et)(OAc)_2\cdot CH(OAc)\cdot O\cdot C_6H_2(OAc)_2\cdot CO_2H,$$

m. p. 154—159° (decomp.), $[\alpha]_D^{19}$ +45·98° in alcohol. The last-mentioned substance is converted by warm dilute pyridine into *d*-penta-acetyl-leucodigallic acid, the acetylation of which by acetic anhydride yields *d*-hexa-acetyl-leucodigallic acid (Abstr., 1910, i, 265). Quantitative experiments on the amount of ethylcarbonatopenta-acetyl-leucodigallic acid obtained from the acetylated tannin indicate that the ratio of digallic acid to leucodigallic acid in the tannin employed is 4 : 1, and therefore the tannin is tetradigalloyl-leucodigallic anhydride. The acetylation of tannin in strongly cooled acetone by keten yields a *polyacetylpolydigalloyl-leucodigallic anhydride*,

$$OAc\cdot[C_6H_2(OAc)_2\cdot CO\cdot O]_x\cdot C_6H_2(OAc)<\begin{matrix}O\cdot CO\cdot C_6H_2(OAc)_2\cdot O\\ CO\cdot O\cdot C_6H_2(OAc)_2\cdot CH\cdot OAc\end{matrix},$$

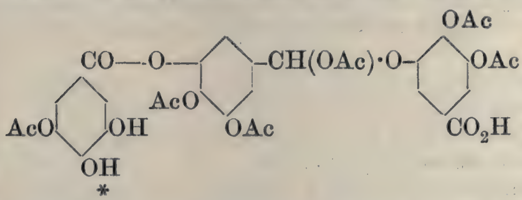
m. p. 287—299° (decomp.), and a trace of the corresponding *acid*. The anhydride is a white, amorphous powder, which is insoluble in cold aqueous sodium hydroxide. It is converted by warm 5% pyridine into *hydroxypolyacetylpolydigalloyl-leucodigallic acid*, which reacts with ethyl chlorocarbonate and *N*/10-potassium hydroxide to form, after acidifying with ice-cold sulphuric acid, *ethylcarbonatopolyacetylpolydigalloyl-leucodigallic acid*, a white, amorphous powder, m. p. 236—244°.

The products obtained by treating tannin, acetylated by keten, with

ethyl chlorocarbonate and aqueous potassium cyanide are triacetylgalloyl cyanide, ethylcarbonatodiacetylgalloyl cyanide (both identified as galloylformic acid), and *diethylcarbonatohexa-acetylgalloyl-leucodigallic acid*,

$$OAc{\cdot}C_6H_2(O{\cdot}CO_2Et)_2{\cdot}CO{\cdot}O{\cdot}C_6H_2(OAc)_2{\cdot}CH(OAc){\cdot}O{\cdot}\underset{CO_2H}{\underset{|}{C_6}}H_2(OAc)_2,$$

m. p. 216—221° (decomp.). When warmed with dilute pyridine, the last substance yields *dihydroxyhexa-acetylgalloyl-leucodigallic acid*, m. p. 257—259° (decomp.), $[\alpha]_D^{17}$ +33·33°, microscopic needles. This acid, which readily yields the corresponding *dimethoxy-acid*, $C_{35}H_{32}O_{19}$, m. p. 219—221° (decomp.), with diazomethane, develops a pronounced green coloration with alcoholic ferric chloride. This indicates that the hydroxyl groups are in ortho-positions relative to one another. Assuming, therefore, that the polydigalloyl-leucodigallic acids are formed by the symmetrical condensation of digallic acid and leucodigallic acid molecules, dihydroxyhexa-acetylgalloyl-leucodigallic acid has the annexed constitution, and its anhydride (and probably, also, polydigalloyl-leucodigallic anhydrides in general) is formed by the elimination of water from the hydroxyl of the carboxyl group and that marked by the asterisk.



C. S.

Tannin, and the Synthesis of Similar Substances. Emil Fischer and Karl Freudenberg (*Ber.*, 1912, **45**, 915—935).—Tannin, after careful purification, when hydrolysed with sulphuric acid yields from 7 to 8% of dextrose, an amount which is undoubtedly somewhat too small on account of the losses during isolation. It is considered that tannin is a compound of 1 mol. of dextrose with 5 mols. of digallic acid, analogous to dextrose penta-acetate and pentabenzoate. This formula is in agreement with the optical activity, molecular weight, weak acidity, and analytical results obtained with tannin.

In confirmation, compounds in every way similar to tannin have been obtained synthetically by combining dextrose with trimethylcarbonatogalloyl chloride in chloroform solution in presence of quinoline. On cautious hydrolysis of this compound with alkali hydroxide, pentagalloylglucose is obtained, which has all the properties of a tannin.

In like manner dextrose has been combined with *p*-hydroxybenzoic acid, also α-methyl glucoside and glycerol with gallic acid.

The crystalline tannin, chebulic acid, also yields dextrose when hydrolysed.

Methods of purifying tannin by extraction with ether, with ethyl acetate, or by means of the potassium salt are described. The value of $[\alpha]_D^{20}$ for different preparations varies around +70°. The acidity is 1/10th that of gallic acid.

Trimethylcarbonatogalloyl chloride has been obtained in quantity in large, colourless crystals, m. p. 91—92° (corr.).

Penta[trimethylcarbonatogalloyl]glucose is a granular, colourless, amorphous powder; it was analysed after drying in a vacuum at 75° over phosphoric oxide. It sinters at about 90°, and begins to decompose at 130°, $[\alpha]_D^{20}$ +34·34° (±0·4°).

Pentagalloylglucose is a yellow, amorphous powder, $[\alpha]_D$ +31° to +35° in water or +44·4° in alcohol. It softens at about 150°, and begins to decompose at 160°. It has an astringent and bitter, but not acid, taste. The aqueous solution precipitates gelatin, and has most of the properties of tannin.

*Penta[*p*-methylcarbonatohydroxybenzoyl]glucose*, prepared by interaction of *p-methylcarbonatohydroxybenzoyl chloride*, dextrose, and quinoline in chloroform solution, is a colourless, easily powdered, amorphous mass, $[\alpha]_D^{20}$ +100°.

*Penta[*p*-hydroxybenzoyl]glucose* is obtained in hard, yellow-coloured, amorphous flakes, $[\alpha]_D^{20}$ +124·3° to 128·8°, on hydrolysis with sodium hydroxide.

Tetra[trimethylcarbonatogalloyl]-α-methyl glucoside is a colourless, amorphous powder, $[\alpha]_D^{20}$ +48·7°.

Galloyl-α-methylglucoside softens at 130°, decomp. 140°, $[\alpha]_D^{20}$ +26·4°; it is similar in properties to pentagalloyl glucose.

Tri[trimethylcarbonatogalloyl]glycerol is a colourless, spongy mass, very similar in properties to the dextrose derivatives. E. F. A.

Gallocarboxylic [Pyrogalloldicarboxylic] Acid. HUGO VOSWINCKEL and FRITZ DE WEERTH. (*Ber.*, 1912, **45**, 1242—1246).—Previous methods for the preparation of pyrogalloldicarboxylic acid gave very unsatisfactory results (compare Sennhofer and Brunner, Abstr., 1881, 267), but it is now found that almost theoretical yields are obtained by heating an intimate mixture of crystallised gallic acid and excess of either potassium or sodium hydrogen carbonate in sealed tubes at 150—160°. Assuming, as usual, that gallic acid is a 3 : 4 : 5-trihydroxybenzoic acid, Sennhofer and Brunner considered pyrogalloldicarboxylic acid to be 3 : 4 : 5-trihydroxy-*o*-phthalic acid, but the fact that acetyl chloride or acetic anhydride entirely fail to produce an anhydride has led the present authors to give it the constitution of a trihydroxy*iso*phthalic acid. Their view is supported by the observation of Feist (Abstr., 1908, i, 101), that a trihydroxyphthalic acid derived from Columba root differed from pyrogalloldicarboxylic acid, and also by the fact that the cotarnic acid of Roser (Abstr., 1889, 418), which is undoubtedly a methoxy-methylenedioxy-*o*-phthalic acid, did readily form an anhydride. Analogous to the observation of Feist that it is extremely difficult to methylate the acid, the authors have found that it entirely resists complete acetylation, and they suggest that it has a ketonic or diketonic structure which might also explain the intense colours of the calcium and barium salts.

Heating the acid with acetyl chloride gave an *acetyl* derivative, $C_8H_5O_7 \cdot C_2H_3O$, which crystallised with ½ mol. acetic acid or with 1 mol. water when reprecipitated from its sodium hydroxide solution; with excess of acetic anhydride a *diacetyl* derivative, $C_8H_4O_7(C_2H_3O)_2$,

was obtained which also separated with $\frac{1}{2}$ mol. acetic acid, but which changed to a mono-acetylated compound in alkaline solution; on melting the acid with its own weight of acetic anhydride and potassium acetate, the carboxyl groups were eliminated, leaving pyrogallol triacetate. J. C. W.

Humic Acids. BRUNO TACKE and H. SÜCHTING (*Landw. Jahrb.*, 1911, **41**, 717—754).—A study of the chemical and physical properties of peat carried out on the lines followed by A. Baumann and E. Gully (*Mitt. Bayr. Moorkulturanstalt.*, Nos. 3 and 4).

Fresh material, and samples dried at varying temperatures and for different periods, was treated with solutions of numerous acids and salts, also with organic solutions, such as gelatin and sugar. The amount of adsorption by the peat, and the chemical changes taking place in the unadsorbed liquid and in the solid were carefully studied, and experimental evidence brought forward to show that humic acids have a definite acid character independent of their colloidal properties.

F. M. G. M.

Preparation of Pentachlorobenzaldehyde. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 243416).—*Pentachlorobenzaldehyde*, needles, m. p. 197—199°, is readily prepared by the action of concentrated or fuming sulphuric acid on pentachlorobenzylidene chloride, pentachlorobenzyl chloride, or the crude mixture obtained by chlorinating pentachlorotoluene at high temperatures. F. M. G. M.

Molecular Compounds as Preliminary Products in Cases of Condensation. II. JULIUS SCHMIDLIN and RUDOLF LANG (*Ber.*, 1912, **45**, 899—912. Compare Abstr., 1910, i, 836).—In the case of organic condensations, by the study of the melting-point curves of mixtures of the two components, proof is afforded of the formation of molecular compounds in the same proportions as those in the condensation product.

Thus 1 mol. of *m*-nitrobenzaldehyde forms a molecular compound with two mols. of benzene, with which it condenses to a triphenylmethane derivative. It does not condense with phenol; in this instance the two branches of the melting-point curve cut in a single eutectic, excluding the formation of a molecular compound.

Two mols. of phenol condense abnormally with two mols. of *p*-hydroxybenzaldehyde, but a molecular compound of the same composition is formed.

The system benzhydrol–phenol shows two maxima corresponding with molecular compounds in the proportions 1 : 1 and 1 : 2. Systems containing dimethylaniline do not afford evidence of the formation of molecular compounds.

The Friedel Crafts' reaction is discussed from this point of view; in many cases aluminium chloride acts as a catalyst, in others it reacts in molecular proportions. In the case of the reaction between benzene and halogen alkyl, it is shown that there is no formation of a binary compound from either of the three components taken in pairs, and it remains only to assume the formation of a ternary compound between

all three components. Such appear to be fairly stable at low temperatures, but liberate hydrogen chloride when warmed.

E. F. A.

[Preparation of Triarylmethane Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 243749).—It is found that halogenated benzene or diphenyl di- or poly-aldehydes condense readily with aromatic hydroxycarboxylic acids to form dyes. The following compounds are described in the original:

2 : 5-*Dichloroterephthalaldehyde*, m. p. 158°; *tetrachloroterephthalaldehyde*, m. p. 193°; 4 : 6-*dichloro*iso*phthalaldehyde*, m. p. 163°; 4 : 4'-*dichloro*-3 : 3'-*dialdehydodiphenyl*, m. p. 204°; 4 : 4'-*dibromo*-3 : 3'-*dialdehydodiphenyl*, m. p. 192°, and 3 : 3'-*dialdehydodiphenyl*-4 : 4'-*disulphonic acid.*

F. M. G. M.

Angeli-Rimini Reaction of the Aldehydes. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 389—393).—The author has now repeated his previous work with the copper salts produced by means of Piloty's acid from anisyl methyl ketone (from anethole glycol) and benzyl methyl ketone (compare Angeli, this vol., i, 117), and finds that they do not give the Angeli-Rimini reaction when the stoichiometric quantity of alkali is employed. To account for the reaction which may be observed when an excess of alkali is used, he suggests an explanation differing from that of Angeli (*loc. cit.*).

R. V. S.

β-Benzyliminopropyl Methyl Ketone. Keto-enol Isomerism. LEOPOLD RÜGHEIMER and G. RITTER (*Ber.*, 1912, 45, 1332—1340).—Acetylacetone and benzylamine interact according to the equation $C_5H_8O_2 + C_7H_9N = C_{12}H_{15}ON + H_2O$. From its behaviour with ferric chloride and the formation of a benzoate, the authors are of opinion that the product is largely, if not entirely, of the structure

$$CH_2Ph{\cdot}N{:}CMe{\cdot}CH{:}CMe{\cdot}OH.$$

The occurrence of two forms of the benzoyl derivative (no isomerism has yet been detected with the parent substance) is ascribed to *cis-trans*-isomerism due to the ethylenic linking. The C:N linking is indicated by the difficulty of reaction between acetylacetone and benzylmethylamine. These results render doubtful the earlier explanations of the isomerism observed with the condensation product of ethyl acetoacetate and benzylamine (Möhlau, Abstr., 1895, i, 140; Hantzsch and von Hornbostel, Abstr., 1898, i, 195).

β-Benzyliminopropyl methyl ketone is obtained by the careful interaction of equimolecular quantities of acetylacetone and benzylamine; the product is a pale yellow oil, b. p. 183—183·5°/17 mm., which can be solidified to tablets, m. p. 24°. It is soluble in sodium hydroxide solution, and gives a coloration with ferric chloride. Attempts to condense the product with another molecule of benzylmethylamine by heating in a sealed tube were unsuccessful, the only isolated product being acetobenzylamide, m. p. 62—66°.

a-Oximino-β-benzyliminopropyl methyl ketone,

$$CH_2Ph{\cdot}N{:}CMe{\cdot}CAc{:}NOH,$$

was obtained by the action of sodium nitrite on the glacial acetic acid solution; it forms colourless crystals, m. p. 126—127°, soluble to a yellow solution in sodium hydroxide solution; it gives no coloration with ferric chloride. Treatment with boiling dilute sulphuric acid gave the γ-oxime of $\beta\gamma\delta$-triketopentane, $OH\cdot N\colon C(COMe)_2$.

Cautious benzoylation of β-benzyliminopropyl methyl ketone yielded a mixture of benzobenzylamide (m. p. 106—107°), with a *substance* of doubtful nature, and two forms of the *benzoyl* derivative. The more easily fusible form (m. p. 119—121°) tends to change into the isomeric form, m. p. 132°. Neither form gives a coloration with ferric chloride, and both are easily hydrolysed by dilute potassium hydroxide solution, giving benzoic acid. D. F. T.

[Preparation of Nitromethylbenzanthrone.] Badische Anilin- & Soda-Fabrik (D.R.-P, 242621).—*Nitromethylbenzanthrone*, m. p. 243°, is prepared by nitrating methylbenzanthrone (m. p. 199°); when heated at 220—240° with sulphur, it furnishes a crystalline, glistening bronze paste, which forms a vat dye. F. M. G. M.

Action of Iodides on Bromoanil. Iodoanil and Some of Its Derivatives. Henry A. Torrey and William H. Hunter (*J. Amer. Chem. Soc.*, 1912, **34**, 702—716).—In an earlier paper (Abstr., 1905, i, 217) it was shown that when bromoanil is heated with a solution of potassium iodide in acetone, dibromodi-iodo-*p*-benzoquinone is produced. A further study of this reaction has shown that in addition to dibromodi-iodo-*p*-benzoquinone, m. p. 258—259°, there are produced tetraiodo-*p*-benzoquinone, bromotri-iodo-*p*-benzoquinone, and iodoanil. Iodoanil can be obtained as the chief product by heating first with alcoholic potassium iodide, and subsequently with alcoholic sodium iodide solution.

*Bromotri-iodo-*p*-benzoquinone*, m. p. 253—254°, crystallises in short, broad, brown, prismatic crystals, and reacts with sodium phenoxide to form bromoiododiphenoxy-*p*-benzoquinone. Iodoanil, m. p. 282—284° (decomp.), forms small, chocolate-coloured needles.

Dibromodi-iodoquinone unites with diphenylamine to form an additive compound, $C_6O_2Br_2I_2,NHPh_2$ (*loc. cit.*), which crystallises in purplish-black needles; its m. p. varies with the rate of heating. By the action of potassium phenoxide on dibromodi-iodo-*p*-benzoquinone, or on bromotri-iodo-*p*-benzoquinone, bromoiododiphenoxy-*p*-benzoquinone, m. p. 282—283°, is produced, together with a small quantity of another substance, which is probably the tetraphenoxy-*p*-benzoquinone described by Jackson and Grindley (Abstr., 1896, i, 155). When a solution of dibromodi-iodo-*p*-benzoquinone in toluene is boiled with a large excess of aniline, there are formed dianilino-*p*-benzoquinone and another substance, which does not melt below 300°, and is probably bromodianilino-*p*-benzoquinone.

When iodoanil is heated with potassium phenoxide solution, it is converted into *di-iododiphenoxy-*p*-benzoquinone*, m. p. 290°. The following compounds were obtained by the action of cresoxides on bromo-, chloro-, and iodo-anil. *Dibromodi-*m*-tolyloxy-*p*-benzoquinone*, m. p. 193°; *dibromodi-*p*-tolyloxy-*p*-benzoquinone*, m. p. 254—263°

(decomp.); *dichlorodi*-p-*tolyloxy*-p-*benzoquinone*, m. p. 254—255°; and *di-iododi*-p-*tolyloxy*-p-*benzoquinone*, m. p. 272—274° (decomp.). When di-iododiphenoxy-*p*-benzoquinone is treated with sodium ethoxide, *di-iododiethoxy*-p-*benzoquinonediethylhemiacetal*, $C_6I_2(OEt)_2(OH\cdot OEt)_2$, is produced, which forms minute, pale yellow crystals. *Di-iododimethoxy*-p-*benzoquinonedimethylhemiacetal* was obtained similarly as a white, amorphous powder.

If iodoanil is treated with excess of sodium methoxide solution and the resulting hemiacetal is treated with *N*-sodium hydroxide, *iodoanilic acid* is produced, which forms yellowish-red, feathery crystals, and begins to decompose at about 205°.

By the action of aniline on di-iododiphenoxy-*p*-benzoquinone, dianilino-*p*-benzoquinone is formed, together with *iododianilino*-p-*benzoquinoneanil*, $C_6HOI(NHPh)_2\colon NPh$, which crystallises in deep yellowish-brown needles, and decomposes at about 225°.

When solid potassium iodide is added to a saturated solution of chloroanil in acetone, the *salt*, $C_6O_2Cl_4,C_6Cl_4(OK)_2$, is produced, which crystallises in green needles, and is hydrolysed by water with formation of a white, amorphous substance, probably the *hemiether*,

$$C_6O_2Cl_4,C_6Cl_4(OH)_2.$$

The *sodium* salt, $C_6O_2Cl_4,C_6Cl_4(ONa)_2$, has a bluish-green colour, and is converted by dilute sulphuric acid into a mixture of chloroanil and tetrachloroquinol. By the action of sodium iodide on a solution of tetrabromo-*o*-benzoquinone in acetone, the *salt*,

$$C_6O_2Br_4,C_6Br_4(ONa)_2,\tfrac{1}{2}CH_3\cdot CO\cdot CH_3,$$

is produced, which forms bluish-green needles, and decomposes at 80°. Similar compounds were obtained from bromoanil and tetrachloro-*o*-benzoquinone. When a mixture of bromoanil, potassium iodide, and alcohol is left at the ordinary temperature, a green salt is not produced, but dibromodi-iodo-*p*-benzoquinone is gradually formed. E. G.

Octaiodoquinhydrone. C. LORING JACKSON and E. K. BOLTON (*Ber.*, 1912, 45, 871—873).—Iodoanil dissolved in benzene, saturated with sulphur dioxide and containing a drop or two of water, was set aside for four weeks, when large, lustrous, black crystals of *octaiodoquinhydrone*, $C_6O_2I_4,C_6(OH)_2I_4$, were deposited; these have decomp. 190°. When it is dissolved in benzene and a little alcohol and the solution is evaporated, a mixture of yellowish-brown iodoanil with colourless tetraiodoquinol is obtained. The latter is also formed when the black crystals are treated with sodium hydroxide and the solution is made acid. E. F. A.

The Melting Point of Anthraquinone. ERNST PHILIPPI (*Monatsh.*, 1912, 33, 373—374).—The m. p. (273°) generally assigned to anthraquinone is too low. Pure anthraquinone has m. p. 285—286° (corr.). This figure agrees with that recorded by Kempf (Abstr., 1908, ii, 929). H. W.

Preparation of α-Hydroxyanthraquinone Alkyl Ethers. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 242379).—α-Hydroxyanthraquinone ethers are readily prepared from the sodium

derivative of the corresponding a-hydroxyanthraquinone by the action of dialkyl sulphates in the presence of a condensing agent.

Erythroxyanthraquinone methyl ether was thus obtained from potassium erythroxyanthraquinone; the quinizarin dimethyl ether has m. p. 170—171° (Lagodzinski, Abstr., 1895, i, 232, recorded 143°).

F. M. G. M.

Preparation of Mercaptans in the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 241985).—When authraquinonediazonium compounds are treated with salts of xanthic acid they yield the corresponding anthraquinonylxanthic esters; these are hydrolysed by alcoholic alkali hydroxides to the corresponding mercaptans.

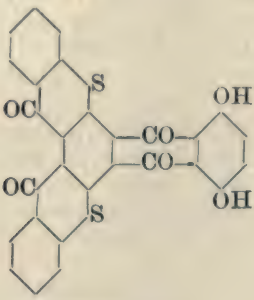
Authraquinone 1-*mercaptan*, prepared from 1-aminoanthraquinone, forms olive-brown flakes, m. p. 187°; the corresponding *anthraquinone 2-mercaptan* has an olive-green colour. F. M. G. M.

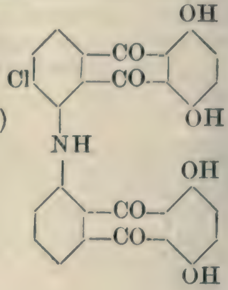
Dichloroquinizarins. M. FREY (*Ber.*, 1912, **45**, 1358—1364).—3 : 6-, 3 : 4-, and 4 : 5-Dichlorophthalic anhydrides react with quinol in the presence of boric acid with the formation of dichlorodihydroxybenzoylbenzoic acids, which, when heated with concentrated sulphuric acid, yield the corresponding dichloroquinizarins.

5 : 8-*Dichloroquinizarin*, $C_6H_2Cl_2{<}^{CO}_{CO}{>}C_6H_2(OH)_2$, crystallises in brownish-red needles, m. p. 266°. Its *diacetyl* derivative has m. p. 170°. When the *potassium* salt of 5 : 8-dichloroquinizarin is heated at 180° with potassium phenoxide and the product acidified, 8-*chloro*-5-*phenoxyquinizarin* is obtained in light red needles, m. p. 243°. Replacement of the second chlorine atom by the phenoxy-group was not observed. It could, however, be replaced by the p-toluidino-group by heating 8-chloro-5-phenoxyquinizarin with p-toluidine in the presence of potassium and copper acetates at 150°, whereby 8-p-*toluidino*-5-*phenoxyquinizarin*, m. p. 278°, is obtained. 5 : 8-*Dianilinoquinizarin*, m. p. 245°, is formed by heating 5 : 8-dichloroquinizarin and aniline with potassium carbonate and copper powder at 150—160°, whilst 1 : 4 : 5 : 8-tetrahydroxyanthraquinone, m. p. 246°, results when 5 : 8-dichloroquinizarin, slaked lime, water, and copper powder are heated at 250° during twenty hours. The *barium* salt, $C_{14}H_4O_6Ba_2$, of the latter was analysed. When 5 : 8-dichloroquinizarin and thiosalicylic acid are boiled in amyl alcoholic solution in the presence of copper and potassium acetates, *quinizarin*-5 : 8-*bis*-o-*thiolbenzoic acid*, m. p. 235°, is obtained, which, when dissolved in nitrobenzene and treated with phosphorus pentachloride and subsequently with aluminium chloride, yields *quinizarin*-5 : 6-7 : 8-*dithioxanthone* (I), m. p. 197—199°, the *barium* salt of which was analysed.

5 : 6-*Dichloroquinizarin*, m. p. 208°, is obtained in the same manner as 5 : 8-dichloroquinizarin. It yields a *diacetyl* derivative, m. p. 140°. When heated with β-aminoanthraquinone in boiling nitrobenzene solution in presence of copper and potassium acetates, it forms 5-*anthraquinonyl*-β-*amino*-6-*chloroquinizarin* (II), m. p. above 300°.

6 : 7-Dichloroquinizarin, m. p. 288°, was similarly obtained in poor yield. Its *diacetyl* derivative has m. p. 125°.

(I.) 

(II.) 

H. W.

Synthesis of Phenanthraquinones. FRITZ MAYER (*Ber.*, 1912, **45**, 1105—1113).—2 : 2′-Dialdehydodiphenyl and 2 : 2′-dialdehydo-6 : 6′-dimethyldiphenyl when warmed with an aqueous alcoholic solution of potassium cyanide are transformed into phenanthraquinone and 4 : 5-dimethylphenanthraquinone (compare Kenner and Turner, Trans., 1911, **99**, 2108). An attempt to apply the same reaction to 2 : 2′-dialdehydo-6 : 6′-dimethoxydiphenyl was unsuccessful.

o-Iodobenzylideneaniline, when heated with copper powder at 160—180°, is converted into 2 : 2′-*dibenzylideneaniline*, m. p. 98—99°, which is transformed by hydrochloric acid into 2 : 2′-dialdehydodiphenyl, m. p. 67° (Kenner and Turner, *loc. cit.*, give m. p. 62°). The latter compound, when heated with aqueous alcoholic potassium cyanide solution, yields phenanthraquinone, m. p. 204—205°, the identity of which was further established by transformation into its monoxime, m. p. 158°.

2-Nitro-3-methoxybenzaldehyde was converted into its oxime, and the latter reduced by ferrous hydroxide to 2-*amino*-3-*methoxybenzaldoxime*, m. p. 136—137°. This, when diazotised and treated with potassium iodide, yielded 2-*iodo*-3-*methoxybenzaldehyde*, m. p. 86—87°, which, when warmed with aniline, gave 2-*iodo*-3-*methoxybenzylideneaniline*, m. p. 107—108°, after previous softening. Treatment of the latter substance with copper powder at 200° led to the formation of 6 : 6′-*dimethoxy*-2 : 2′-*dibenzylideneaniline*, from which, by the action of hydrochloric acid, 2 : 2′-*dialdehydo*-6 : 6′-*dimethoxydiphenyl*, m. p. 120°, was obtained. No definite product was isolated from the action of aqueous alcoholic potassium cyanide solution on this substance.

A precisely similar series of reactions, with 2-nitro-3-methylbenzaldehyde as starting point, yielded the following compounds: 2-*amino*-3-*methylbenzaldoxime*, m. p. 127°; 2-*iodo*-3-*methylbenzaldehyde*, m. p. 83—84°; 2-*iodo*-3-*methylbenzylideneaniline*, m. p. 73°; 2 : 2′-*dialdehydo*-6 : 6′-*dimethyldiphenyl*, m. p. 111°. The latter substance, when heated with an aqueous alcoholic solution of potassium cyanide, formed 4 : 5-*dimethylphenanthraquinone*, m. p. 222—223°.

The action of potassium cyanide on *iso*phthalaldehyde led to the formation of a *substance*, the analyses of which agreed with the formula $C_{16}H_{12}O_4,H_2O$, but in which the presence of water of crystallisation could not be confirmed. Oxidation with potassium permanganate in alkaline solution yielded *iso*phthalic acid. H. W.

Preparation of Santalol and Menthol Ethers. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 242421).—When santalol or menthol (or their sodium derivatives) in toluene solution or suspension is treated with chloromethyl ether in the presence of dimethylaniline (or other indifferent base), compounds of therapeutic value are produced.

Methoxymethylsantalol, $C_{15}H_{23}\cdot O\cdot CH_2\cdot OMe$, a colourless liquid, b. p. 152—158°/4 mm., evolves formaldehyde when heated with dilute mineral acid.

Methoxymethylmenthol, $C_{10}H_{19}\cdot O\cdot CH_2\cdot OMe$, has b. p. 100—102°/7 mm. F. M. G. M.

Isomeric Tanacetyl Alcohols and Thujenes. LEO A. TSCHUGAEFF and W. FOMIN (*Ber.*, 1912, **45**, 1293—1298. Compare Tschugaeff, Abstr., 1900, i, 129; 1901, i, 38; 1904, i, 515).—Tanacetyl alcohol, prepared from commercial tanacetone, has been resolved by the recrystallisation of the cinchonine salt of tanacetyl hydrogen phthalate. From the less soluble fraction was isolated a tanacetyl alcohol, D_4^{20} 0·9187, $[\alpha]_D$ +116·93° (compare Paolini, Abstr., 1911, i, 730). The substance in the mother liquors was converted into a sparingly soluble strychnine salt, from which, after recrystallisation, a solid tanacetyl alcohol was obtained, m. p. 28°, $[\alpha]_D$ −9·12° (in toluene).

The *d*-rotatory alcohol yielded an unstable and, to all appearances, homogeneous xanthate, which on decomposition gave apparently pure α-thujene, b. p. 151°/759 mm., D_4^{20} 0·8301, n_D^{20} 1·45150, α_D −37·20.

The *l*-rotatory alcohol gave a more stable xanthate, by the decomposition of which a thujene was obtained (presumably β-), b. p. 147°/739 mm., D_4^{20} 0·8208, n_D^{20} 1·44708, $[\alpha]_D$ +110·78°. D. F. T.

The Constituents of Ethereal Oils. I. ψ-Cedrol, a Physical Isomeride of Cedrol. II. Certain Sesquiterpene Alcohols. III. Tetrahydrocaryophyllene. FRIEDRICH W. SEMMLER and ERWIN W. MAYER (*Ber.*, 1912, **45**, 1384—1394).—All specimens of cedar wood oil contain the primary alcohol cedrenol, $C_{15}H_{24}O$, and cedrene. Many specimens contain also the solid tertiary alcohol cedrol, $C_{15}H_{26}O$. In addition, the authors have isolated from the fractions of high b. p. a new, liquid, saturated, tertiary alcohol, $C_{15}H_{26}O$, which they name *ψ-cedrol*.

For the preparation of the latter, cedar wood oil was fractionated, the fraction of higher b. p. treated with phthalic anhydride and the unattacked portion again distilled. In this manner, a pale green oil, b. p. 147—152°/9 mm., D^{20} 0·9964, α_D^{20} +21·5°, n_D^{20} 1·5131, was prepared, from which no solid substance could be obtained. Apparently, therefore, solid cedrol was not present in the oil employed. ψ-Cedrol reacts readily with sodium. With acetic

anhydride it yields an *acetate*. When oxidised, it does not yield a ketone. When heated with zinc dust, it gives a mixture of cedrene and *dihydrocedrene*, from which the latter substance was isolated after treatment of a solution of the mixture in chloroform with ozone. It has b. p. 106—115°/10 mm. (mainly 109—112°/10 mm.), D^{20} 0·907, a_D + 37°, n_D^{20} 1·4882. A second *dihydrocedrene*, b. p. 122—123°/10 mm., D^{20} 0·9204, a_D^{20} + 2°, n_D^{20} 1·4929, was obtained by reduction of cedrene by means of hydrogen in the presence of platinum.

The alcoholic nature of ψ-cedrol was further proved by the action of formic acid on it, whereby cedrene was obtained, the physical constants of which agreed with those of the natural cedrene. The identity of the two compounds was confirmed by the oxidation of artificial cedrene to cedreneketonic acid and cedrenedicarboxylic acid, and transformation of the latter compound into its dimethyl ester. These compounds were identical with those prepared by Semmler and Risse (Abstr., 1912, i, 201) from natural cedrene.

II. According to Sandurin (Abstr., 1909, i, 98), guaiol is a tertiary alcohol. The authors, from the determination of its density and molecular refraction, draw the conclusion that it is a bicyclic alcohol with one double bond. Oxidation of it in aqueous acetone by means of potassium permanganate yielded the corresponding *glycerol*, $C_{15}H_{28}O_3$, m. p. 210—211°. Ozonisation in glacial acetic acid solution and subsequent decomposition of the ozonide yielded neutral and acidic products. From the former, a stable, light yellow *oil*, $C_{14}H_{20}O_3$, b. p. 138—144°/7 mm., D^{20} 0·9972, a_D^{20} + 96°, n_D 1·5276, which appears to be an oxide, and a *keto-lactone*, $C_{15}H_{24}O_3$, b. p. 200—208°/8 mm., D^{20} 1·067, n_D^{20} 1·5005, were isolated.

From the fractions of higher b. p. prepared by distilling oil of carnations, a *sesquiterpene alcohol*, $C_{15}H_{26}O$, was obtained. It has b. p. 138—148°/8 mm., D^{20} 0·9681, a_D − 17°, n_D 1·5010, and is apparently a bicyclic alcohol with one double bond. Phosphorus pentachloride converts it into the *chloride*, $C_{15}H_{25}Cl$, b. p. 147—155°/12 mm., D^{20} 0·990, from which, by treatment with alcoholic potash, the *hydrocarbon*, $C_{15}H_{24}$, b. p. 123—126°/10 mm., D^{20} 0·9273, a_D^{20} − 23°, n_D^{20} 1·5024, was obtained.

III. In order to decide whether the same carbon skeleton is present in natural and "regenerated" caryophylline (Semmler and Mayer, Abstr., 1911, i, 73), both hydrocarbons were reduced by hydrogen in the presence of platinum. The tetrahydrocaryophyllene obtained in each case was identical. H. W.

Bornylene. Leo Tschugaeff and W. Budrick (*Annalen*, 1912, **388**, 280—293).—The researches of Jotsitsch (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 542), Bredt (Abstr., 1909, i, 498), and Kondakoff (*ibid.*, 1910, i, 327), have raised the question of the individuality of bornylene. The present paper deals with the examination of the bornylene obtained from methyl *l*-bornyl xanthate. The purest *d*-bornylene, obtained by the decomposition of the xanthate at 176—177°, and sublimation and distillation over sodium of the product, followed by fractional distillation, purification by alcohol, and finally rectification over sodium, has b. p. 146·5°/750 mm., m. p. 109—109·5°,

$[\alpha]_C$ 15·06°, $[\alpha]_D$ 19·29°, $[\alpha]_E$ 25·49°, $[\alpha]_F$ 31·06°, and $[\alpha]_F/[\alpha]_C$ 2·06 (compare Bredt, *loc. cit.*). Its oxidation in benzene by 1% aqueous potassium permanganate yields about 73% of *l*-camphoric acid ; this is the only acidic product of the oxidation, camphenic and camphenilic acids (the formation of which would indicate the presence of some camphene) being specially, but unsuccessfully, sought for. The oxidation in a similar manner of a similarly prepared *l*-bornylene yields *d*-camphoric acid as the only acidic product. These camphoric acids are optically individual, indicating that the respective bornylenes do not contain *r*-bornylene.

When bornylene in benzene is exhaustively oxidised by 1% aqueous potassium permanganate, the products which are volatile with steam contain a small quantity of a hydrocarbon, $C_{10}H_{16}$, b. p. 153—153·5°, m. p. 64·5—65°, which is shown to be cyclene by direct comparison.

From the preceding experiments, therefore, it is seen that the active bornylene obtained by the decomposition of the methyl bornyl xanthate is a mixture of the active bornylene with a very little cyclene, and that racemisation does not occur during the decomposition.

C. S.

Approximate Value of the Molecular Weight of Caoutchouc. Paul Bary (*Compt. rend.*, 1912, 154, 1159—1160).—A study of the equilibrium between sulphur and caoutchouc during vulcanisation (Abstr., 1911, i, 1003) gives $(C_{10}H_{16})_nS_2$ as the formula for vulcanised rubber. Analysis shows that the minimum proportion of combined sulphur after vulcanisation is 2·5%, whence $n = 18·4$, a number in good agreement with Weber's formula, $C_{200}H_{320}S_2$. The molecular weight of the material at the temperature of vulcanisation is, therefore, approximately $136 \times 20 = 2720$.

W. O. W.

The Colloidal Nature of Caoutchouc. Felix Ahrens (*Chem. Zeit.*, 1912, 36, 505—506).—Emulsions of rape oil and water may be prepared, in which either the oil or the water forms the closed phase. There must, therefore, be an intermediate point, at which the two liquids are in more intimate contact. It is in fact found that in emulsions of a certain concentration the oil globules become coated with a fine foam, and this very stable foam protects the globules against oxidation when a current of oxygen is passed in, provided that the temperature is not allowed to rise. In the latex, the caoutchouc globules are suspended in serum, and oxygen is always present, usually amounting to 2%. The globules take up this oxygen at the surface, and so form a protecting layer. If this layer is chemically or mechanically destroyed after coagulation, it is not re-formed, owing to the absence of the requisite constituents of the serum. The presence of this layer accounts for the reticulated structure of caoutchouc.

If two portions of dry washed Para rubber are taken, one is kneaded between close rollers, and two 8% solutions in benzene are prepared from them, the kneaded specimen becomes liquid in a few months, owing to the destruction of the protecting layer, whilst the untreated specimen is not altered.

C. H. D.

Amygdalins and their Inter-reactions with Emulsin. VERNON K. KRIEBLE (*J. Amer. Chem. Soc.*, 1912, **34**, 716—735).—It was shown by Walker and Krieble (Trans., 1909, **95**, 1437) that the rotation of a racemised amygdalin solution is independent of the nature and of the concentration of the alkali, and that the equilibrium point is independent of the temperature and of the concentration of the amygdalin. It was also found that racemic amygdalin could be partly resolved into its optical isomerides, and that when a racemised solution was evaporated to dryness on the water-bath the specific rotation was increased.

It is now shown that a minute trace of hydroxyl ions is capable of effecting the racemisation of amygdalin, and that the cyano-group is necessary for the change to take place. *r*-Amygdalin is composed of 56·25% of the *d*-form, and 43·75% of the *l*-form. The increase in rotation when racemic solutions are heated to dryness on the water-bath is due to a very small amount of hydroxyl ions produced by the hydrolysis of the barium salt of an unknown acid, minute quantities of which are always associated with amygdalin. The change giving rise to the increased rotation is a transformation of the cyano-group. The cause having been ascertained, it was easily removed, and it was then possible to isolate pure *d*-amygdalin, the properties of which closely resemble those of the *l*-form. *d*-Amygdalin, like the *l*-modification, is hydrolysed by emulsin into benzaldehyde, dextrose, and hydrogen cyanide, but at a slower rate. The *r*-form is hydrolysed more slowly than the *l*- and *d*-forms separately.

It has been shown by previous workers that emulsin, not only hydrolyses active benzaldehydecyanohydrin, but also synthesises it from hydrogen cyanide and benzaldehyde. Whilst Feist, Rosenthaler, and Auld found that *d*-benzaldehydecyanohydrin was always present in the hydrolytic solutions, the author has found that with certain specimens of emulsin, *l*-benzaldehydecyanohydrin was invariably obtained. With benzaldehyde and hydrogen cyanide, the *d*-form is obtained, which agrees with the results of the investigators mentioned. E. G.

Strophanthus Glucosides from Various Sources. ARTHUR HEFFTER and FRITZ SACHS (*Biochem. Zeitsch.*, 1912, **40**, 83—124).—The authors give a detailed account of the literature of the various strophanthins (*Kombé*, *Hispidus*, and *Gratus*) which have been prepared, and call attention to the fact, that the botanical origin of many of the preparations which have been described is uncertain. For this reason they have confined their attention to the *Strophanthus hispidus* and *Strophanthus Kombé*, using materials of known origin, which had been submitted previously to botanical investigation. An amorphous product was obtained both from the hispidus and Kombé varieties in the following way: The residue from the alcoholic extract was taken up by water, the aqueous solution was clarified by the addition of lead acetate, the excess of lead separated from the filtrate of the lead salt, and the liquid was then evaporated down in the presence of excess of calcium carbonate. After evaporation to a syrup, the calcium carbonate was filtered off, and a large excess of

ammonium sulphate was added. The glucoside was precipitated, and was purified by repeated solution in alcohol and precipitation from the alcoholic solution by ether. From the hispidus plant, the glucoside had the rotation $[\alpha]_D + 13 \cdot 9°$, and from the Kombé plant $[\alpha]_D$ was $+ 11 \cdot 87°$. Both yielded on hydrolysis a strophanthidin with $[\alpha]_D$ about 41°. The pharmacological investigation, analyses, and methoxyl estimation of the glucosides from the two sources indicated that these substances were identical. In addition to these, the authors also succeeded in obtaining a crystalline glucoside from the Kombé plant. This was got by heating the calcium carbonate, after evaporation of the mixture (see above), with hot water. From the solution thus obtained, needles separated on cooling; it was recrystallised from hot water. The substance appears to be identical with that previously described by Arnaud. It contains 61·93% carbon, 7·64% hydrogen, and 4·73% methoxyl, and has $[\alpha]_D + 28 \cdot 72°$. It yields on hydrolysis strophanthidin, and differs from the amorphous products in that it has a slight hæmolytic action; otherwise the pharmacological action is very similar. All the products prepared give a green colour with concentrated sulphuric acid, which is in contrast with the pink colour obtained by some other authors with the strophanthin of different origins. S. B. S.

Oxidation of Some Ketohydrofurans. GEORGES DUPONT (*Compt. rend.*, 1912, 154, 987—989. Compare Abstr., 1911, i, 554, 804; this vol., i, 290).—Potassium permanganate oxidises ketotetramethyltetrahydrofuran, forming *tetramethyldiglycollic acid*, $O(CMe_2 \cdot CO_2H)_2$, m. p. 153—155°; the *lead* salt crystallises with $3 \cdot 5H_2O$; the *diethyl* ester has b. p. 114°/13 mm., D^{16} 1·0173, n_D 1·4292 (compare Jungfleisch and Leroux, Abstr., 1908, i, 127).

Ketodimethyldiethyltetrahydrofuran undergoes oxidation by potassium permanganate, giving *dimethyldiethyldiglycollic acid*,

$$O(CMeEt \cdot CO_2H)_2,$$

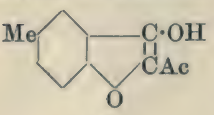
m. p. 155°; the *lead* salt is anhydrous, and decomposes at about 210°. At the same time an *isomeride* of the acid is formed, having m. p. 90—92°; the *lead* salt has m. p. 252° (decomp.). Ketodimethyltetrahydrofuran is oxidised in the same way, giving rise to a syrupy acid, b. p. 132—133°/12 mm., D^{18} 1·1316, n_D 1·4282; this is probably *β-hydroxyacetylbutyric acid*. W. O. W.

The *aci*-Nitro-derivative of Ketotetramethyltetrahydrofuran. GEORGES DUPONT (*Compt. rend.*, 1912, 154, 1176—1178).—Ketotetramethyltetrahydrofuran is added to the calculated amount of fuming nitric acid. After several days crystals are obtained, having m. p. 71—72° when crystallised from light petroleum, but which separate from benzene in large needles, m. p. 78—79°. The two varieties have the same chemical properties, but determinations of their refractive indices show the first modification to be aci-*nitroketotetramethyltetrahydrofuran*, $O\!\!<\!\!\begin{array}{l}CMe_2 \cdot C{:}NO_2H \\ CMe_2 \cdot CO\end{array}$, whilst the second is the true *nitro*-derivative. The compound is strongly acid, and forms well-defined salts. The *potassium*, *sodium*, and *ammonium* salts crystallise in leaflets, and when added to aqueous solutions of salts of other metals give

crystalline and often highly coloured precipitates. The salts of *calcium*, *barium* (with $2H_2O$), *zinc*, *copper*, *mercurous* (yellow), *mercuric*, *lead* (yellow), *ferrous* (violet, with $2H_2O$), *ferric* (brown), *nickel* (yellowish-green), *cobalt* (rose), *manganese* (golden-yellow, with $3H_2O$), *chromium* (yellow), *tin*, *antimony*, *cadmium*, and *uranium* (golden-yellow) have been prepared.

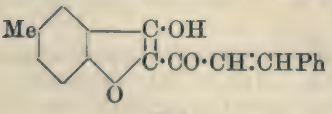
Nitroketotetramethylhydrofuran distils in a vacuum, but decomposes when heated under ordinary pressure, in accordance with the equation: $2C_8H_{13}O_4N = C_8H_{12}O_3 + 2COMe_2 + H_2O + 2CO + N_2$. In addition to acetone and water, the liquid distillate contains *diketo*-2 : 2 : 5 : 5-*tetramethyltetrahydrofuran*, $\begin{matrix}CO\cdot CMe_2\\ | \\ CO\cdot CMe_2\end{matrix}\!\!>\!O$, a red liquid, b. p. about 170°. When exposed to moist air this compound takes up $2H_2O$, forming colourless crystals, m. p. about 80°. The *dioxime* volatilises without melting at about 240°. W. O. W.

The C-Acyl Derivatives of 2-Hydroxycoumarones. KARL AUWERS (*Ber.*, 1912, **45**, 976—994).—The 2-hydroxy-1-acylcoumarones (Auwers, Abstr., 1910, i, 629) in their behaviour towards reagents for the carbonyl group resemble the aromatic *o*-hydroxyketones; they differ, however, in their greater tendency to form additive compounds. Methylation by methyl sulphate appears to be a direct substitution, producing stable O-ethers, whilst the action of methyl iodide and sodium methoxide is not so simple, giving C-methyl derivatives which immediately split into simpler molecules.

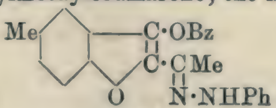


(I.)

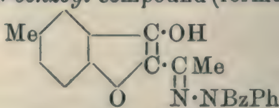
2-Hydroxy-1-acetyl-4-methylcoumarone (formula I annexed), recrystallised from light petroleum or precipitated by acid from alkaline solution, forms slender needles, m. p. 87—89°; it separates from hot methyl alcohol, however, in compact crystals, m. p. 104°; a mixture of the two modifications has the higher m. p., and even at the ordinary temperature the form of lower m. p. slowly isomerises. Treatment of this substance with acetyl chloride and pyridine forms the *acetyl* derivative; the acetyl group is less stably fixed than the benzoyl group in the corresponding benzoic ester, for the latter with semicarbazide yields a semicarbazone (m. p. 220°), whilst the former yields only the semicarbazone of the original hydroxyacetylmethylcoumarone. The *benzylidene* compound (formula II) forms yellow needles, m. p. 119°. The phenylhydrazone (described earlier) forms a *benzoyl* derivative (formula III), yellow needles, m. p. 179—180°, which is also obtained by the action of phenylhydrazine on the already described benzoate of the hydroxyacetylmethylcoumarone; the isomeric N-*benzoyl* compound (formula IV)



(II.)



(III.)



(IV.)

is obtained by the interaction of the hydroxyacetylmethylcoumarone with *as*-benzoylphenylhydrazine hydrochloride; it is a yellow, crystalline powder, m. p. 186°.

Methylation by methyl sulphate in the presence of alkali yields 2-*methoxy*-1-*acetyl*-4-*methylcoumarone*, colourless needles, m. p. 98—99°; the *semicarbazone* of this ether forms yellow needles, m. p. 240°, the *phenylhydrazone*, needle crystals, m. p. 129°, and the *benzylidene* derivative, yellow needles, m. p. 131—133°; the semicarbazone is smoothly hydrolysed by oxalic acid solution to the original ether, but 30% sulphuric acid gives 2-hydroxy-4-methylcoumarone,

$$C_6H_3Me{<}{\genfrac{}{}{0pt}{}{C(OH)}{O}}{>}CH$$

(m. p. 51—52°). Semicarbazones can be methylated by methyl sulphate, for example, the semicarbazone of 4-hydroxy-*m*-tolyl methyl ketone (needles, m. p. 221—225°) gives the *methyl ether*, colourless needles, m. p. 199°, b. p. 254°/760 mm., 132°/11 mm.; similarly, the semicarbazone of hydroxyacetylmethylcoumarone gives as main product the semicarbazone of the methyl ether (see above), together with an *isomeride*, yellow needles, m. p. 172—173°; the latter is converted into the former (m. p. 240°) on warming with glacial acetic acid.

2-*Methoxy*-1-*benzoyl*-4-*methylcoumarone* is obtained (like the corresponding acetyl compound) by the action of methyl sulphate; it forms slender needles, m. p. 77—78°.

The action of methyl iodide and sodium methoxide converts hydroxyacetylmethylcoumarone into 2-*hydroxy*-1 : 4-*dimethylcoumarone*, $C_6H_3Me{<}{\genfrac{}{}{0pt}{}{C(OH)}{O}}{>}CMe$, an oil, b. p. 125°/15 mm., which slowly crystallises in needles, m. p. 63°; it is very feebly acidic, and has a clinging odour.

The identity of this substance was confirmed by a synthesis from *p*-tolyl methyl ether and bromopropionyl bromide in the presence of aluminium chloride; the primary product, o-*α*-*chloropropionyl*-p-*cresol*, $OH{\cdot}C_6H_3Me{\cdot}CO{\cdot}CHMeCl$, m. p. 84—85·5°, passes easily into the above hydroxydimethylcoumarone. The substance is very stable towards alkalis or acids, but is oxidised by permanganate to methylsalicylic acid. With an equimolecular quantity of semicarbazide, the substance gives the *semicarbazone*, $O{<}{\genfrac{}{}{0pt}{}{C_6H_3Me}{CHMe}}{>}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 191°, which is hydrolysed to the parent substance by 30% sulphuric acid; excess of semicarbazide gives a *substance*, m. p. 225°, formed by the condensation of one molecule with two of semicarbazide.

Methyl iodide and sodium methoxide act on the semicarbazone of 2-hydroxy-1-acetyl-4-methylcoumarone, giving some hydroxyacetyl 1 : 4-dimethylcoumarone (above), together with the O-methyl ether of the semicarbazone (above), and a colourless substance forming compact needles, m. p. 223°; the last-named with sulphuric acid gives dimethylcoumarone (m. p. 63°), and so must be a C-*methyl* derivative, but otherwise the structure is uncertain; methylation by methyl sulphate converts it into a *substance*, crystallising in needles, m. p. 192°.

Methylation of 2-hydroxy-1-benzoyl-4-methylcoumarone by methyl iodide and sodium methoxide gives the O-methyl ether (above),

together with methyl salicylate and hydroxy-1 : 4-dimethylcoumarone.

D. F. T.

Preparation of O-Alkyl and C-Alkyl Derivatives. KARL AUWERS (*Ber.*, 1912, 45, 994—997. Compare preceding abstract).—Other substances have been investigated to discover how far the characteristic difference in behaviour towards methyl sulphate and methyl iodide extends.

Substances of the types $C_6H_4{<}\begin{matrix}C(OH)\\ O\end{matrix}{>}C\cdot CO_2R$,

$$C_6H_4{<}\begin{matrix}C(OH)\\ S\end{matrix}{>}C\cdot CO_2R,$$

and $C_6H_4{<}\begin{matrix}C(OH)\\ NH\end{matrix}{>}C\cdot CO_2R$ react with methyl sulphate, giving O-ethers, whilst with alkyl halides they primarily give products of the type $C_6H_4{<}\begin{matrix}CO\\ O(S)\end{matrix}{>}C{<}\begin{matrix}R\\ CO_2R'\end{matrix}$, accompanied by some O-derivative. It is not yet certain whether the difference is to be ascribed to the alkylation agent or to the reaction conditions (for example, the medium, etc.).

β-Diketones do not easily form O-ethers with methyl sulphate; for example, acetylacetone gave quite negative results, whilst benzoylacetone gave phenyl ethyl ketone (from the splitting of the primary $COPh\cdot CHMe\cdot COMe$), together with an O-*methyl ether*, probably

$$COPh\cdot CH\!:\!CMe\cdot OMe,$$

b. p. 154—155°/16 mm.

D. F. T.

Synthesis of *o*-Hydroxyflavone. A. PISTERMANN and JOSEF TAMBOR (*Ber.*, 1912, 45, 1239—1242).—Of the eight possible monohydroxyflavones, Kostanecki and his pupils have already prepared six (compare Abstr., 1898, i, 369; 1899, i, 370; 1900, i, 669; 1901, i, 558; 1904, i, 764; 1907, i, 75), whilst *o*-hydroxyflavone is the subject of this paper and the remaining 8-hydroxyflavone is being studied.

Methyl *o*-methoxybenzoate and *o*-ethoxyacetophenone were condensed to 2-methoxy-2′-ethoxybenzoylacetophenone, an oily β-diketone which could not be crystallised, but which boiling concentrated hydriodic acid converted into 2′-*hydroxyflavone*, $C_6H_4{<}\begin{array}{l}O-C\cdot C_6H_4\cdot OH\\ \quad\;\; \|\\ CO\cdot C\end{array}$, crystallising from alcohol in light yellow, shining needles, m. p. 238·5°. This gave a pale yellow solution in strong sulphuric acid, but an intense yellow one in dilute alkalis, whilst the *acetyl* derivative, $C_{17}H_{12}O_4$, formed pale yellow needles, m. p. 90°, and the 2′-*methoxyflavone*, $C_{16}H_{12}O_3$, crystallised in colourless needles, m. p. 105°.

Similarly, *o*-ethoxyacetophenone has been coupled with ethyl acetate and with ethyl propionate, the crude 2-*ethoxyacetylacetophenone*, $C_{12}H_{14}O_3$, being an oil, which crystallised from dilute alcohol in colourless needles, m. p. 56—57°, and was converted by hot hydriodic acid into the 2-methylchromone of Bloch and Kostanecki (Abstr., 1900, i, 502); the o-*ethoxypropionylacetophenone*, $C_{13}H_{16}O_3$, also

formed colourless needles, m. p. 46°, but did not give a crystallisable product with hydriodic acid. J. C. W.

Action of Hydrogen Peroxide on Bromothiophens. MAURICE LANFRY (*Compt. rend.*, 1912, **154**, 1090—1092. Compare Abstr., 1911, i, 740, 1009).—The bromothiophens are much more resistant to the action of hydrogen peroxide than thiophen itself, and in no case do they yield a sufficient amount of oxythiophens (*loc. cit.*) for identification. Monobromothiophen is decomposed by hydrogen peroxide with liberation of bromine and formation of dibromothiophen. The latter is less easily decomposed, whilst tri- and tetra-bromothiophen are unaltered by the reagent. W. O. W.

Preparation of Derivatives and Substitution Products of 3-Keto-(1)-thionaphthens. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 242461).—The action of carbonyl chloride on indoxyl has been described previously (Abstr., 1911, i, 675); it is now found that a similar condensation takes place when a cooled aqueous alkaline solution of 3-keto-(1)-thionaphthen (its homologues or substitution products) is treated with carbonyl chloride. The *product* forms glistening red, leaflets, m. p. 123—125°. F. M. G. M.

[Preparation of "Tetramethylthioindigo."] KALLE & Co. (D.R.-P. 242998).—When 4-carboxy-*m*-xylyl-5-thiolacetic acid (this vol., i, 126) is heated at above 100° with moist sulphuric acid, it yields "*tetramethylthioindigo*" without sulphonation; the same reaction also takes place when phosphoric or boric acids are employed.

F. M. G. M.

Preparation of Berberine Derivatives. MARTIN FREUND (D.R.-P. 242573. Compare Abstr., 1900, ii, 588; 1905, i, 657).—When α-benzyldihydroberberine methiodide (Abstr., 1905, i, 151) is warmed in dilute alcoholic solution with excess of ammonium hydroxide, it furnishes a *base*, a crystalline powder, m. p. 187—188°; this when reduced with a lead cathode in dilute sulphuric acid at 20—25° (or with tin and concentrated hydrochloric acid) is converted into a *base*, forming yellow, rhombic tablets, m. p. 163°, containing C = 75% and H = 6%, and yielding crystalline *salts*. iso*Butyldihydroberberine*, yellow leaflets or needles, m. p. 112—113°, was prepared from berberine hydrochloride and *iso*butyl bromide by Grignard's reaction; it furnishes a *methiodide*, yellow needles, m. p. 200° (decomp.), which, when treated with excess of ammonium hydroxide (or sodium carbonate), yields a *base*, $C_{25}H_{29}O_4N$, brownish-yellow prisms, m. p. 146°. This base when electrolytically reduced is converted into two *bases*, one consisting of yellow, rhombic tablets, m. p. 155—157°, which does not combine with methyl iodide; the other, colourless crystals, m. p. 175—176°, yields a *methiodide*, m. p. 246°. F. M. G. M.

Preparation of Tetrahydroberberine Derivatives. MARTIN FREUND (D.R.-P. 242217. Compare Abstr., 1907, i, 632; 1905, i, 657; this vol., i, 383).—Contains details of the preparation of compounds previously described.

a-Ethyltetrahydroberberine methiodide has m. p. 229°, and by the action of silver hydroxide, as previously described (*loc. cit.*), yields a *base*, m. p. 130—131°. F. M. G. M.

Crystallisation of Quinine and Quinine Trihydrate. Jules Ville (*Bull. Soc. chim.*, 1912, [iv], 11, 398—400).—Anhydrous quinine has been obtained in the form of minute, colourless lamellæ by passing air containing ammonia into a solution of quinine hydrobromide maintained at 100°. The alkaloid sublimes slightly at 165—167°, and melts at 172—173°. Quinine trihydrate separates in long silky needles when enough dilute ammonia to produce faint opalescence is added to a solution of quinine hydrobromide in acetone and water, and the mixture is set aside. The trihydrate melts at 89—90° when projected on a heated mercury surface; it loses part of its water in the air, and is completely dehydrated over sulphuric acid, T. A. H.

[Rearrangement of Cinchonine and Quinine into their Poisonous Isomerides, Cinchotoxine and Quinotoxine.] Paul Rabe (*Ber.*, 1912, 45, 1447—1449).—This rearrangement (Abstr., 1911, ii, 33) had been previously described by Biddle (compare this vol., i, 296). C. S.

Dihydrohydrastinine: the Stereochemistry of Compounds Containing Nitrogen. Martin Freund and Keita Shibata (*Ber.*, 1912, 45, 855—861).—By the action of ethylene bromide, magnesium, and ether on hydrastinine, two isomeric dihydrohydrastinines are obtained. The stable isomeride, m. p. 163°, crystallises in silky, lustrous, pointed prisms; the *hydrobromide* crystallises in slender needles, m. p. 238—239° (decomp.); the *hydriodide* separates in needles aggregated in rounded bunches, m. p. 238—239° (decomp.); the *hydrochloride* crystallises in platelets and prisms; the *sulphate* crystallises in platelets, m. p. 255—256°.

The stereoisomeric iso*dihydrohydrastinine*, m. p. 175—176°, crystallises in rhombic plates or prisms. It is converted into the stable form when melted; the mixture of the two forms sinters at 144°, m. p. 155—156°. The *hydrobromide* crystallises in needles, m. p. 212—213°; the *hydriodide* forms bunches of needles, m. p. 207—208°; the *hydrochloride* crystallises in plates; the sulphate separates in needles, m. p. 250—251°.

Dihydrohydrastinine forms an *hydrogen tartrate* crystallising in needles, m. p. 158—159°; the isomeric acid tartrate could not be obtained in crystalline form. Neither isomeride could be resolved into optically active *d*- and *l*-forms, and they are regarded as internally compensated inactive meso-forms.

The monomethiodide of dihydrohydrastinine crystallises in prisms, m. p. 218°; it is basic and forms a hydriodide crystallising in rhombic plates, m. p. 205—206°; the methiodide of the *iso*-base separates in rhombic plates and prisms, m. p. 235—236°, and gives a hydriodide crystallising in rhombic plates, m. p. 228—229°.

N-*Methyldeisodihydrohydrastinine* crystallises in well-formed, mono-

clinic plates, m. p. 175—176°; the *hydriodide* has m. p. 151—152°. It forms an additive compound with methyl iodide with difficulty; the *methiodide* crystallises in needles, m. p. 189—190° (decomp.).

N-Methyldedihydrohydrastinine was obtained as an oil readily reacting with methyl iodide to form a methiodide, which loses trimethylamine on treatment with alkali. E. F. A.

Morphine. XXIII. Preparation and Hydrolysis of an Iodocodeide. LUDWIG KNORR and WALTER HARTMANN (*Ber.*, 1912, **45**, 1350—1353).—The hydrolysis of the so-called α-chlorocodeide yields ψ-codeine and smaller quantities of *allo*-ψ-codeine and *iso*codeine (Knorr and Hörlein, Abstr., 1908, i, 361), complex atomic rearrangements taking place which obscure conclusions as to the composition of the halogen codeides. α-Iodocodeide has therefore been prepared, in the hope that the iodine atom would be replaceable at a lower temperature than the chlorine atom, but even when hydrolysis took place at the ordinary temperature, the same complicated changes occurred as with the chloro- and bromo-compounds.

α-Iodocodeide was prepared by heating α-chlorocodeide with potassium iodide in ethyl alcoholic solution. It forms light orange needles, which soften at about 167°, and have m. p. about 200°. In chloroform solution it has $[\alpha]_D^{20}$ +136·5° (c=3·95). Its *hydriodide*, m. p. 180—182°, is very characteristic.

When hydrolysed by acetic acid, it yields ψ-codeine and *allo*-ψ-codeine (isolated as hydriodides) and *iso*codeine (isolated as hydrogen oxalate). The same products were obtained when the hydrolysis was performed with silver acetate and acetic acid. H. W.

Morphine. XXIV. Methods of Preparation of Ethers of ψ-Codeine. LUDWIG KNORR and WALTER HARTMANN (*Ber.*, 1912, **45**, 1354—1358).—The codeine methyl ether obtained by Knorr and Roth (Abstr., 1911, i, 1014) by the action of sodium methoxide on a methyl alcoholic solution of α-chlorocodeide differs from that obtained by Pschorr and Dickhaüser (Abstr., 1911, i, 908), and is to be considered as the methyl ether of ψ-codeine (compare previous abstract). Such ethers of ψ-codeine are readily obtained by heating α-chlorocodeide with alcohols.

ψ-Codeine methyl ether is obtained by heating α-chlorocodeide with methyl alcohol at 100—110° during two days in yield of 40—50%. *ψ-Codeine ethyl ether*, prepared in a similar manner, has m. p. 76°. Its *hydrochloride*, $C_{20}H_{25}O_3N,HCl,\frac{1}{2}EtOH$, forms white needles, m. p. about 255° (decomp.). Its *hydriodide* decomposes at 267—270°. *ψ-Codeine propyl ether* yields a *hydriodide*, m. p. about 259° (decomp.), but could not be obtained in the crystalline state. *ψ-Codeine phenyl ether* (prepared by H. Hörlein) is obtained by boiling α-chlorocodeide and sodium phenoxide with absolute alcohol, and has m. p. 187°. *ψ-Codeine* p-*tolyl ether*, obtained similarly, has m. p. 165°, $[\alpha]_D^{20}$ −13·7° (c=2·78) in chloroform solution. Its *hydrochloride* has m. p. 231°, whilst its *nitrate* decomposes at 180—181°. *ψ-Codeine* m-*tolyl ether* and its *nitrate* have m. p. 144° and 192° respectively, whilst *ψ-codeine* o-*tolyl ether* melts at 189° after previous softening. *ψ-Codeine guaiacyl*

ether, prepared from sodium ethoxide, guaiacol, and α-chlorocodeide, has m. p. 214°, and forms beautiful crystalline salts, such as the *hydrochloride*, *nitrate*, decomposing at about 197°, *hydrogen oxalate*,

$$C_{25}H_{27}O_4N,H_2C_2O_4,$$

m. p. 197°, and *hydrogen tartrate*, $C_{25}H_{27}O_4N,C_4H_6O_6$, m. p. 205°. H. W.

Constitution of *iso*Narcotine and the Synthesis of Narcotine Derivatives of High Molecular Weight. MARTIN FREUND and KARL FLEISCHER (*Ber.*, 1912, 45, 1171—1182).—In cases where opianic acid reacts as a lactone, the authors suggest that the expression opian(lact) should be employed. The compounds now described are of this type.

Bromohydrocotarnine, in which the active hydrogen atom in position 5 is replaced by bromine, could not be condensed with opianic acid. Accordingly, *iso*narcotine is regarded as 5-opianyl hydrocotarnine. Narcotine also contains the hydrogen atom in position 5, and condenses with opianic acid to a mixture of stereoisomeric α- and β opianylnarcotines, $C_{32}H_{31}O_{11}N$.

The methiodide of the α-isomeride is converted by silver oxide into an ammonium base, which concentrated alkali hydroxide splits to form an amino-acid, $C_{33}H_{37}O_{13}N$, α-(5)-opianylhydratenarceine.

Narcotine condenses with formaldehyde, forming methylenedinarcotine, a lævorotatory, crystalline compound. On oxidation, methylenedicotarnine is formed, which, like cotarnine, forms crystalline salts which give yellow solutions.

*iso*Narcotine does not condense with formaldehyde. Cotarnine also could not be condensed with formaldehyde or with opianic acid, although hydrocotarnine reacts with both of these.

α-Opianylnarcotine crystallises in radially-grouped aggregates of very slender needles, m. p. 199°, $[\alpha]_D^{12}$ −94·73°. The salts with mineral acids are oily; with concentrated sulphuric acid a violet-red coloration is obtained.

β-Opianylnarcotine forms slender, colourless needles, m. p. 173—175°, $[\alpha]_D^{12 \cdot 5}$ −103·6°.

α-Opianylnarcotine forms a *methiodide*, crystallising in lustrous, colourless platelets, which begin to change at 210°, m. p. 233°.

The *picrate* separates in yellow, microscopic, rectangular plates, m. p. 217°.

The *methiodide* of the β-isomeride forms a pale yellow powder without lustre, which sinters at 200°, decomp. 222°.

By the action of dilute nitric acid on α-opianylnarcotine, a *compound*, crystallising in slender, yellow needles, m. p. 206° (decomp.), is obtained.

α-(5)-*Opianylhydratenarceine* crystallises in colourless, matted needles, which change at 180°, decomp. 193°.

Methylenedinarcotine forms a colourless, dusty, crystalline powder, which colours at 200°, m. p. 215—216°, $[\alpha]_D$ −93·4°, and gives a faint yellow coloration with concentrated sulphuric acid, changing to a dirty red on the addition of a drop of dilute nitric acid, and then decolorising immediately. The *methiodide* was obtained as an oil

solidifying to an amorphous mass. The *picrate* forms a crystalline, yellow powder changing at 165°, decomp. 173°; in sunlight it turns a sealing-wax red.

Methylenedicotarnine hydrobromide crystallises in yellow, prismatic rods, m. p. 240° (decomp.); the *free base* is a yellowish-white powder, m. p. 132° (decomp.). The *hydriodide* crystallises in deep yellow rods, decomp. 235°. E. F. A.

Methylenedihydrocotarnine. MARTIN FREUND and ADOLF DAUBE (*Ber.*, 1912, 45, 1183—1186).—The compound described as hydrodicotarnine by Bandow (Abstr., 1897, i, 581), and obtained by the action of sulphuric acid on hydrocotarnine, contains in reality a CH_2 group more than stated by Bandow. It is obtained quantitatively by the action of formaldehyde and sulphuric acid on hydrocotarnine, and is properly termed methylenedihydrocotarnine. No such condensation takes place with bromohydrocotarnine, in which bromine replaces the active hydrogen.

Methylenedihydrocotarnine, $CH_2{:}\left[C_6(OMe)(CH_2O_2){<}\begin{matrix}CH_2\cdot NMe\\ | \\ CH_2\cdot CH_2\end{matrix}\right]_2$,

has m. p. 211—212°. The hydrobromide crystallises in platelets, m. p. 240—244° (Bandow, *loc. cit.*, gives 218—220°). The hydroiodide forms colourless needles, m. p. 242° (Bandow gives 227—229°); the *dichromate* separates in reddish-yellow plates. The *dimethiodide* crystallises in yellow needles, which soften at 267°. E. F. A.

Action of Aldehydes on Pyrrole Substances. Pyrogenetic Decomposition of Derivatives of Dipyrrylmethane. U. COLACICCHI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 410—415. Compare Abstr., 1911, i, 1030).—The present paper deals chiefly with the decomposition by heat of the product from paracetaldehyde and 3-acetyl-2 : 4-dimethylpyrrole, previously described.

Both at the ordinary and at reduced pressure this substance yields on distillation the same two products, namely, 5-acetyl-2 : 4-dimethylpyrrole and a substance, $C_9H_{13}ON$, which forms small, lustrous needles, m. p. 160°, and is probably 5-acetyl-2 : 3 : 4-trimethylpyrrole. In addition 3-acetyl-2 : 4-dimethylpyrrole is also formed in smaller quantity. In the decomposition, therefore, not only is the ethylidene linking broken, but the position of the acetyl group is changed. When 3-acetyl-2 : 4-dimethylpyrrole is heated in a sealed tube it is transformed quantitatively into the isomeride with the acetyl group in position 5.

When oximinoacetylacetone is reduced by Knorr's method in the presence of methyl ethyl ketone, 5-acetyl-2 : 3 : 4-trimethylpyrrole is not formed, but instead diacetyldimethylpyrazine, m. p. 98°. By reducing methyl ethyl ketoxime in the same way in the presence of acetylacetone, however, 5-acetyl-2 : 4 : 5-trimethylpyrrole, m. p. 209—210°, is obtained, and since this substance is not identical with the acetyltrimethylpyrrole obtained in the above dry distillation, it is probable that that derivative has the constitution assigned above.

When 3-acetyl-2 : 4 : 5-trimethylpyrrole is treated with hydrazine hydrate, the corresponding ketazine is obtained, m. p. above 280°.

R. V. S.

Detection of *l*-Proline as a Primary Product of Protein Hydrolysis. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1912, **78**, 96—114).—Emphasis is laid on the difficulty of isolating and purifying proline, particularly on the unsatisfactory nature of the solubility in alcohol as a criterion of purity. The conclusion is drawn that at present there is no satisfactory method of estimating the amount of pure proline contained in the decomposition products of a protein.

The fact that proline is a primary product of protein hydrolysis is definitely proved by its direct isolation as hydantoin from the products of fermentative hydrolysis of casein or gelatin or from the contents of the intestine. 0·5 Gram of the recrystallised proline hydantoin, m. p. 140°, was obtained from the intestine of five dogs.

E. F. A.

Esterification of the Monoamino-acids by means of Ethyl Iodide. Separation of Pyrrolidenecarboxylic Acid from Glutamic Acid. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1912, **78**, 115—127).—The silver salt of pyrrolidonecarboxylic acid is readily esterified by ethyl iodide, whereas, under like conditions, glutamic acid, aspartic acid, asparagine, and proline remain unaltered. It is thus possible to separate pyrrolidonecarboxylic acid from admixture with glutamic or other amino-acids.

Attempts to prove by this method the presence of pyrrolidonecarboxylic acid in the products of digestion of casein led to the isolation of an ester, which could not be identified, but which formed glutamic acid hydrochloride when hydrolysed with hydrochloric acid.

Ethyl pyrrolidenecarboxylate (Fischer and Boehner, Abstr., 1911, i, 484; Abderhalden and Weil, Abstr., 1911, i, 1049) crystallises in needles or platelets, m. p. 60—61·5°.

Proline forms a very unstable silver salt, which soon becomes black, especially when warmed with water.

E. F. A.

Glutamic and Pyrrolidonecarboxylic Acids. III. Mercury Salts, Pyrrolidonyl Chloride, and Pyrrolidonylamide. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1912, **78**, 333—343).—Glutamic acid gives a bulky, white precipitate on the addition of mercuric acetate solution. Pyrrolidonecarboxylic acid gives no such precipitate, and it is hoped to separate the two acids in this way.

Mercuric glutamate, $CH_2<\begin{matrix}CH(NH_2)\cdot CO_2\\CH_2\text{——}CO_2\end{matrix}>Hg$, forms a heavy, sandy, crystalline powder; heated in a capillary, it has decomp. 208—209°.

Mercuric pyrrolidonecarboxylate, $4(C_5H_6O_3N)_2Hg,3HgO$, resembles gypsum, and has decomp. 207—208°.

Pyrrolidonyl chloride, prepared by the interaction of thionyl chloride

with the carboxylic acid, forms colourless crystals; it is decomposed by water, giving pyrrolidonecarboxylic acid. By the action of ammonia in chloroform, *dl*-pyrrolidonylamide is obtained, m. p. 220—221° (corr.). This is also formed in small quantities on heating the ammonium salt of glutamic acid. E. F. A.

Preparation of Phonopyrrolecarboxylic Acid from Hæmin. HANS FISCHER and ERICH BARTHOLOMÄUS (*Ber.*, 1912, **45**, 1315—1316).—Phonopyrrolecarboxylic acid, which can be obtained from hæmatoporphyrin by reduction (Piloty, Abstr., 1909, i, 858; 1911, i, 92), is also obtainable in good yield by the reduction of hæmin. The phonopyrrolecarboxylic acid is separated first as the picrate (decomp. 163°), from which the free substance (colourless needles, m. p. 125—126°) is liberated by dilute sulphuric acid. D. F. T.

Complex Chromium Fluorides. III. N. COSTĂCHESCU (*Ann. Sci. Univ. Jassy*, 1912, **7**, 87—100).—*Trifluorotripyridinechromium*, $\left[Cr^{F_3}_{Py_3}\right]$, is obtained by heating sixteen grams of violet hexaaquochromium fluoride with 200 grams of pyridine on the water-bath for two hours. After collecting the green precipitate which is formed, the filtrate is concentrated until slender, violet crystals of the desired compound begin to separate. These can be dried in an atmosphere of pyridine, after which they are stable in the air. The crystals are readily soluble in water, giving a violet, neutral, non-conducting solution which does not contain fluoridion. On prolonged boiling the aqueous solution becomes blue in colour, after which a grey product is deposited containing two molecules of pyridine; finally, the green, hydrated chromium fluoride separates.

Trifluorotripyridinechromium hydrate, $\left[Cr^{F_3}_{Py_3}\right],H_2O$, is prepared by heating 25 grams of the violet compound, $[Cr(H_2O)_6]F_3,3H_2O$, with 180 grams of pyridine under reflux on a water-bath until the solid has almost dissolved. An intense blue solution is obtained, which, after separation from the green solid formed and further concentration, deposits dark blue crystals of the required hydrate. A further quantity of these crystals can be obtained by extracting the green solid with chloroform. They are readily soluble in water, the solution possessing properties similar to that of the anhydrous compound. When the solution in chloroform is evaporated on the water-bath at a temperature just below the boiling point of water, *trifluoroaquodipyridinechromium*, $\left[Cr\begin{matrix}Py_2\\H_2O\\F_3\end{matrix}\right],H_2O$, is deposited as a greyish-violet powder, which is soluble in water to a neutral solution possessing a slight conductivity.

Difluorotetrapyridinechromium nitrate, $\left[Cr^{Py_4}_{F_2}\right]NO_3$, is obtained by the interaction of violet chromium fluoride, potassium nitrate, and pyridine. Prolonged heating on the water-bath is necessary, until the dark violet solution first formed changes to a lighter colour; after

filtering and concentrating the solution, the nitrate is deposited as violet crystals, which are soluble in water. The aqueous solution possesses a conductivity corresponding with that of a binary salt. By double decomposition with the appropriate potassium or sodium salts, the following compounds were obtained: The *thiocyanate*, YSCN, where $Y = \left[Cr_{F_2}^{Py_4}\right]$, as violet needles; the *iodide*, YI, as a rosy-violet, crystalline powder; the *ferricyanide*, $Y_3FeC_6N_6$, in large, garnet-red crystals; the *nitroprusside*, $YNa\left[Fe_{(CN)_5}^{NO}\right]$, $4H_2O$, as strawberry-red lamellæ; and the *platinichloride*, Y_2PtCl_6, $6H_2O$, as brick-red, slender needles or leaflets.

Ammines corresponding with the above pyridine compounds could not be obtained. T. S. P.

Complex Iron Salts. N. Costăchescu and G. Spacu (*Ann. Sci. Univ. Jassy*, 1912, 7, 132—138).—The authors have succeeded in isolating the compound formed between ferrous chloride and pyridine in a pure condition (compare Reitzenstein, Abstr., 1900, i, 162; Pfeiffer, Abstr., 1902, i, 175) by the interaction of ferrous chloride and excess of pyridine at $-15°$ in an atmosphere of carbon dioxide. The reaction takes three to four days for completion, at the end of which time canary-yellow crystals of *tetrapyridineferrous chloride*, $[FePy_4]Cl_2$, are obtained. They change on exposure to the air, and on solution in water a greenish precipitate is produced, which changes to a red colour. With a concentrated solution of ammonium thiocyanate, the yellow tetrapyridineferrous thiocyanate is produced (compare Grossmann, Abstr., 1906, i, 7). The solution in 1·19 hydrochloric acid, when saturated with hydrogen chloride at $-18°$, gives crystals of the compound $FeCl_3$,PyHCl (compare Christensen, Abstr., 1906, i, 875).

When exposed in a desiccator for two or three months to the action of concentrated sulphuric acid, tetrapyridineferrous chloride gives slender, acicular crystals of a *compound*, $FePyOCl_2$, to which it is difficult to assign a constitution, and which dissolves in water without decomposition, giving a strongly acid, red solution.

The *compound*, $[Fe_23PyHCl]Cl_6$, is formed by dissolving the tetrapyridine chloride in a small quantity of 1·19 hydrochloric acid and keeping the filtered solution in a desiccator over concentrated sulphuric acid. If forms monoclinic, yellow crystals, having m. p. 125—128°. The aqueous solution possesses a considerable conductivity. If the tetrapyridine chloride is dissolved in hydrobromic acid (D 1·38) and the solution allowed to evaporate spontaneously in the air, reddish, garnet-coloured, monoclinic crystals, showing violet in reflected light, of the *compound*, $\left[Fe_23PyHBr\right]_{Br_4}^{Cl_2}$, are obtained. When these crystals are again dissolved in hydrobromic acid and the solution allowed to evaporate very slowly, large, reddish, garnet-coloured crystals of the *compound*, $[Fe_23PyHBr]Br_6$, are obtained. The corresponding iodides could not be prepared. T. S. P.

Relation Between the Colour and Constitution the Pyridine Dyes from Secondary Aromatic Amines. WALTER KÖNIG and G. A. BECKER (*J. pr. Chem.*, 1912, **85**, [ii], 353—385. Compare this vol., i, 306).—In view of the many analogies existing between the dyes of the triphenylmethane and pyridine-series, a systematic examination of the latter is being undertaken. The present communication deals with the dyes from aromatic secondary amines of the methylaniline type, and cyclic secondary amines, such as dihydroindole and tetrahydroquinoline.

The absorption spectra of the dyes in alcoholic solution are recorded, and the colours, obtained by dyeing cotton mordanted with tannin, have been determined by means of Kallab's colour-analyser (*Zeitsch. angew. Chem.*, 1908, **21**, 1637).

Dyes derived from amines of the methylaniline type are yellow or orange in colour, and show general absorption, whilst those derived from cyclic secondary amines are reddish-orange to violet in colour, and give well-marked absorption bands. In the case of dyes obtained from cyclic amines containing a five-membered ring, it is found that gradual diminution of the thickness of the solution causes the central absorption band to become divided, but this is not the case with those derived from amines containing a six-membered ring. In view of the ease with which the dyes may be prepared, it is suggested that these differences might be utilised to determine whether an amine contains a five or six-membered ring.

The influence of substitution on the colour of the dyes is discussed and interpreted from the point of view of Kaufmann's theory of the divisibility of the valency bond.

The majority of the dyes mentioned below were prepared by the addition of the amine (2 mols.) in alcoholic solution to a freshly prepared mixture of pyridine (1 mol.) and cyanogen bromide (1 mol.) in ether. In a few instances the preparation was effected by heating the amine with 2 : 4-dinitrophenylpyridinium chloride in alcohol solution. Many of the dyes crystallise with water or alcohol, which is often very firmly retained.

The *dye* from *N*-methyl-*o*-toluidine, $C_{21}H_{25}N_2Br,H_2O$, forms a light yellow powder, m. p. 218°; that from N-methyl-*m*-toluidine,

$$C_{21}H_{25}N_2Br,EtOH.$$

red needles, m. p. 83°; the corresponding para-*isomeride* also crystallises with alcohol in red needles, m. p. 140°. The *dye* from N-methyl-*m*-xylidine, $C_{23}H_{29}N_2Br,H_2O$, is a dark yellow powder, m. p. 125°.

N-*Methyl*-o-*anisidine*, prepared from *o*-anisidine and methyl sulphate in nitrobenzene solution, and purified by means of the *nitroso*-derivative, has m. p. 33·5°, and yields a *dye* which could not be obtained in a pure condition.

N-Methyl-*p*-anisidine, prepared from *p*-anisidine and methyl sulphate in ethereal solution (compare Fröhlich and Wedekind, Abstr., 1907, i, 410), has b. p. 130°/15 mm., m. p. 33°, forms a *zincichloride*, crystallising in lustrous leaflets, m. p. 91°, and yields a *dye*, $C_{21}H_{25}O_2N_2Br$, which crystallises in lustrous, brown leaflets, m. p. 45°.

The *dye* from N-methyl-*p*-phenetidine, $C_{23}H_{29}O_2N_2Br$, forms wooly masses of soft, red needles, m. p. 137°; that from N-ethylaniline,

$C_{21}H_{25}N_2Br,H_2O$, red needles, m. p. 91°; that from N-ethyl-*p*-toluidine, $C_{23}H_{29}N_2Br$, red, microscopic leaflets, m. p. 112°; that from N-ethyl-α-naphthylamine (b. p. 168°/14 mm.), $C_{29}H_{29}N_2Br$, a green powder, m. p. 98°; that from N-ethyl-β-naphthylamine, dark red leaflets, m. p. 64°.

Propylaniline forms a *nitroso*-derivative, m. p. 76° (compare Wacker, Abstr., 1888, 466), and a *dye*, $C_{23}H_{29}N_2Br$, which crystallises in dark red needles, m. p. 110°. The *dyes* from *iso*propylaniline, *iso*butylaniline, and *iso*amylaniline could not be obtained in a pure condition. Allylaniline yields a *dye*, $C_{23}H_{25}N_2Br,H_2O$, crystallising in deep red leaflets, m. p. 56°.

N-*Allyl*-p-*anisidine*, prepared from *p*-anisidine and allyl bromide and purified by means of the *nitrosoamine*, has b. p. 260°, and yields a *dye*, $C_{25}H_{29}O_2N_2Br$, crystallising in small, flexible, red leaflets, m. p. 98°.

The *dye*, $C_{21}H_{21}N_2Cl$, obtained from dihydroindole and 2 : 4-dinitrophenylpyridinium chloride, forms a red powder, m. p. 195°.

2-Methyldihydroindole yields with cyanogen bromide a *dye*,

$$C_{23}H_{25}N_2Br,4H_2O,$$

crystallising in violet leaflets, m. p. 154°; with 2 : 4-dinitrophenylpyridinium chloride, the *dye*, $C_{23}H_{25}N_2Cl$, m. p. 125°.

2 : 5-*Dimethyldihydroindole*, prepared by reduction of 2 : 5-dimethylindole, is a yellow oil, b. p. 235—237°; it forms a *platinichloride* (decomp. 208°) and a bluish-red, crystalline *dye*, $C_{25}H_{29}N_2Br$, m. p. 145°.

2 : 6-*Dimethylindole*, obtained by condensing *m*-tolylhydrazine with acetone and fusing the resulting hydrazone with zinc chloride, crystallises in lustrous, silvery leaflets, m. p. 52°, b. p. 153°/11 mm., 273° under ordinary pressure, and is possibly identical with one of the dimethylindoles, described by Dennstedt (Abstr., 1889, 401); on reduction with zinc and hydrochloric acid it yields 2 : 6-*dimethyldihydroindole*, as a yellow oil, b. p. 237—239°, which forms a red crystalline *dye*, $C_{25}H_{29}N_2Br$, m. p. 105°, with previous sintering at 95°.

The *dye* from 3-methyldihydroindole, $C_{23}H_{25}N_2Br,H_2O$, forms reddish-violet, microscopic crystals, m. p. 230°; that from 2 : 3-dimethyldihydroindole, $C_{25}H_{29}N_2Br$, a fiery-red, crystalline powder, m. p. 188°.

2-*Methyl*-3-*ethyldihydroindole*, prepared by reducing the corresponding indole with zinc and hydrochloric acid and purified by means of the *nitrosoamine*, is a yellow oil, b. p. 251—252°, and yields a *dye*, which forms glistening, green crystals, m. p. 115°.

The *dye*, $C_{29}H_{33}N_2Br$, from carbazoline forms dark red crystals, m. p. 175°. α-Methyldihydro-β-naphthindole yields a *dye*, m. p. 194° (not sharp), which was not obtained in a pure condition.

The *dye* from tetrahydroquinoline, $C_{23}H_{25}N_2Br,H_2O$, crystallises in light red leaflets, m. p. 195°; that from 6-methyltetrahydroquinoline, $C_{25}H_{29}N_2Br$, in vivid red leaflets, m. p. 206°.

7-Methylquinoline is reduced by zinc and hydrochloric acid to 7-*methyltetrahydroquinoline*, a pale yellow oil, b. p. 143°/18 mm., which yields a *dye*, $C_{25}H_{29}N_2Br$, crystallising in red leaflets, m. p. 205°. The *dye*

from 8-methyltetrahydroquinoline forms a green, crystalline powder, sintering at 75°; that from 6-methoxytetrahydroquinoline,

$$C_{25}H_{29}O_2N_2Br,$$

violet leaflets, m. p. 213°; that from 2-methyltetrahydroquinoline, $C_{25}H_{29}N_2Br$, vivid red crystals, m. p. 135°; from 2 : 6-dimethyltetrahydroquinoline, $C_{27}H_{33}N_2Br,H_2O$, red needles, m. p. 126°.

The *dye* from tetrahydro-α-naphthaquinoline, m. p. 151°, is green in colour, and could not be obtained pure. The *dye* from tetrahydro-β-naphthaquinoline, $C_{31}H_{29}N_2Br$, crystallises in red leaflets, m. p. 223°; that from α-methylphenmorpholine (2-methyl-2 : 3-dihydro-1 : 4-benzoxazine) [Stoermer, Abstr., 1897, i, 473] in bluish-red crystals, m. p. 205°.

o-*Nitro*-p-*tolyloxyacetone*, $C_{10}H_{11}O_4N$, prepared by condensing chloroacetone with *o*-nitro-*p*-cresol, crystallises in colourless prisms, m. p. 75°. It is reduced by zinc and hydrochloric acid to α-m-*dimethylphenmorpholine* (2 : 7-*dimethyl*-2 : 3-*dihydro*-1 : 4-*benzoxazine*),

$$C_6H_4Me\!<\!\begin{matrix}O\text{—}CH_2\\ NH\cdot CHMe\end{matrix},$$

which has b. p. 145°/11 mm., 162°/21 mm., and is accompanied by p-*chloro*-α-m-*dimethylphenmorpholine* (6-*chloro*-2 : 7-*dimethyl*-2 : 3-*dihydro*-1 : 4-*benzoxazine*). The last-mentioned compound crystallises in white leaflets, m. p. 135°, and yields a *dye*, $C_{23}H_{23}O_2N_2Cl_2Br$, crystallising in red prisms, m. p. 241°.

The *dye*, $C_{25}H_{29}O_2N_2Br$, from *α-m*-dimethylphenmorpholine forms dark red crystals, m. p. 195°.

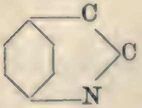
Tetrahydroquinoxaline yields a *dye*, $C_{21}H_{23}N_4Cl,H_2O$, which sinters at 135°. F. B.

Betaines of Nipecotinic Acid and of Pipecolic Acid. Kiyohisa Yoshimura (*Zeitsch. physiol. Chem.*, 1912, 78, 156—158).—The *dimethylbetaine* of *nipecotinic acid*, $C_8H_{15}O_2N$, consists of hygroscopic prisms, which have a sweet taste and react neutral to aqueous solution. The *aurichloride*, $C_8H_{15}O_2N,HAuCl_4$, forms golden-yellow prisms or columns, m. p. 240—244° (decomp.). The *hydrochloride* crystallises in colourless prisms, m. p. 285—287° with frothing. The *picrate* consists of large prisms or columns, m. p. 175—176° (decomp. 240°).

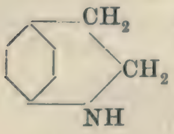
The *dimethylbetaine* of *pipecolic acid* is a neutral, hygroscopic syrup, which does not taste sweet. The *aurichloride*, $C_8H_{15}O_2N,HAuCl_4$, forms lustrous, golden-yellow, four-sided plates, m. p. 238—240° (decomp.). The *hydrochloride* forms prismatic crystals, m. p. 224—225°. The *picrate* crystallises in tiny platelets, m. p. 181—182° (decomp. 235°). E. F. A.

Cyclic Imines. V. Dihydro-*p*-indole and *p*-Indole. Julius von Braun [with W. Gawrilow] (*Ber.*, 1912, 45, 1274—1288).—The failure of Kipping (Trans., 1888, 21) and of Manoukian (Abstr., 1901, i, 528) to bridge over two carbon atoms other than in the ortho-position in the benzene ring has given rise to the view that one aromatic nucleus will only unite with a second in that position. The opinion of the author that the nature of the open chain which is to be linked up with the benzene nucleus is of supreme importance, and his

experience of the easy formation of a nitrogen seven-membered ring in homohydrocarbostyril (Abstr., 1907, i, 524), and of the great ease with which open chain bases which contain chlorine form cyclic imines, have led him to try to build up a ring of the annexed type, with the result that he has succeeded in preparing dihydro-*p*-indole. For this purpose pure *β-chloro-4-aminophenylethane*, $CH_2Cl\cdot CH_2\cdot C_6H_4\cdot NH_2$, was obtained by reducing Barger's nitro-derivative (Trans., 1909, **95**, 2193) by means of stannous chloride, as a yellowish-brown oil with camphor-like odour. The *hydrochloride*, $C_8H_{11}NCl_2$, is almost identical in form with the hydrochloride of the *β-chloro-2-aminophenylethane*, obtained by hydrolysing β-chloro-*o*-benzylaminophenylethane (Abstr., 1911, i, 747); they both melt at 205°, but mixed together, at 150—160°. The *platinichlorides* show a difference, that from the para-base crystallising from hot water in red needles, m. p. 192°, whilst the other decomposes in hot water and melts at 195°, a mixture melting below 190°; similarly with the *benzoyl* derivatives; the para-compound melts at 128°, the ortho- at 120°, and a mixture at 103—105°. The *para*-base is also characterised by a *picrate*, $C_8H_{10}NCl,C_6H_3N_3O_7$, m. p. 155°, which is very sparingly soluble in cold alcohol. That the substances do really belong to the para-series is further evidenced by the formation of hordenine from the nitro-derivative (Barger, *loc. cit*), and by the conversion of the base into p-*β-chloroethylphenol*, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2Cl$, which, like *p*-hydroxychloroacetophenone, and unlike *o*-chloropropylphenol or *o*-hydroxychloroacetophenone, is only slightly volatile in steam, but may be distilled without loss of hydrogen chloride, b. p. 158—163°/10 mm., and is readily transformed into tyrosol. Unlike *o*-β-bromoethylphenol, which readily undergoes ring formation to hydrocoumarone in cold alkali (Störmer and Kahlert, Abstr., 1901, i, 536), the *p*-β-chloroethylphenol is only altered on heating, and yields an impure product, which is not volatile in steam; similarly, *p*-γ-chloropropylphenol (to be described later) does not give a chroman in the way that the ortho-compound does (compare Braun and Steindorff, Abstr., 1905, i, 294).



The failure to produce a para-ring containing oxygen is remarkable in view of the fact that the β-chloro-*p*-aminophenylethane when diluted with ether spontaneously changes into the desired dihydro-*p*-indole, but even here the influence of alkali is to prevent ring formation. The *dihydro*-p-*indole* (annexed formula) is a colourless liquid, which soon darkens when exposed to air, boils at 228—230°, and is very similar to the ordinary ortho-compound, the physical constants being almost identical; and the various derivatives are so much alike that only depressions of the melting points of the mixed substances indicate any difference. The *hydrochloride*, C_8H_9NH,HCl, melts at 217°, that of the ortho-base at 219°; the yellow *platinichlorides*, m. p. 211°; *picrates*, *o*-, m. p. 174°, *p*-, m. p. 177°; *methiodides*, *o*-, m. p. 192°, *p*-, 189°; the p-*benzoyl* derivative, m. p. 118°; and also the p-*benzenesulphonyl* compound, $C_8H_8N\cdot SO_2Ph$, m. p. 130°, insoluble in alkali, have been prepared.



The benzoyl derivative yields with phosphorus pentachloride a chlorobenzoylaminophenylethane, m. p. 128°, which depresses the melting point of *o*-chloro- but not that of the para-isomeride. The dihydro-*p*-indole ring is very stable, resisting the action of concentrated hydrochloric acid in sealed tubes at 180°. When distilled with silver sulphate, it furnishes an indole which is so nearly like ordinary indole that it cannot be said with certainty that it is the para-compound; only a mixture of the picrates shows a depressed melting point, 170—174° instead of 175°. J. C.W.

New Method of Preparation of Substituted Indoles. WALTER MADELUNG (*Ber.*, 1912, **45**, 1128—1134).—A simple and apparently general method of preparing 2-substituted indoles consists in heating about equal quantities of an acyl-*o*-toluidide and sodium alkyloxide for a few minutes at 360—380° in a current of hydrogen, and decomposing the product (sodium derivative ?) with water. The yield is better the greater is the molecular weight of the sodium alkyloxide; thus aceto-*o*-toluidide and sodium ethoxide yield 60% of 2-methylindole, and benzo-*o*-toluidide and sodium ethoxide yield 60% of 2-phenylindole. Indole itself cannot be thus prepared from form-*o*-toluidide.

2:2′-*Di-indyl*, $C_6H_4<\genfrac{}{}{0pt}{}{CH}{NH}>C\cdot C<\genfrac{}{}{0pt}{}{CH}{NH}>C_6H_4$, m. p. about 300° (decomp.), is obtained in 15—20% yield by heating oxalo-*o*-toluidide and sodium amyloxide (rather more than 4 mols.), containing a little amyl alcohol, at 360—380° in a current of hydrogen for about five minutes, distilling off the amyl alcohol, and decomposing the residue with water. It forms yellow crystals, yields a *picrate*,

$$C_{16}H_{12}N_2,2C_6H_3O_7N_3,$$

decomp. 178°, brown needles with a violet shimmer, develops a bluish-black coloration in the pine shaving reaction and an orange coloration with concentrated sulphuric acid, and gives a red coloration with glacial acetic acid and hydrogen peroxide. C. S.

Disruption of the Scatole Ring by means of Phosphorus Pentachloride. JULIUS VON BRAUN and G. KIRSCHBAUM (*Ber.*, 1912, **45**, 1263—1266).—In order to prepare alcohols and aldehydes with branched polymethylene chains and to compare them with those in which the side-chain is not substituted (compare Abstr., 1912, i, 265), the applications of the Grignard reaction mentioned previously (this vol., i, 433) may be used. These give rise to fatty aromatic compounds which are methylated in the 4 or 5 position with regard to the benzene nucleus, but not such as contain the methyl group nearer the ring. The present paper describes a method for the production of α-methyl derivatives.

Following the process for the transformation of quinoline into γ-phenylpropyl chloride (Abstr., 1910, i, 843), 3-methylindole has been reduced (compare Wenzing, Abstr., 1887, 957), the 3-methyldihydroindole converted into the *benzoyl* compound,

$$C_6H_4<\genfrac{}{}{0pt}{}{CHMe}{-NBz-}>CH_2,$$

a well defined substance which crystallises from hot alcohol, m. p.

102°, and undergoes disruption when heated with phosphorus pentachloride at 115—120°. The *o-β-chloroisopropylbenzanilide*,

$$COPh\cdot NH\cdot C_6H_4\cdot CHMe\cdot CH_2Cl,$$

thus obtained is almost insoluble in light petroleum, but dissolves freely in acetone, and crystallises from a mixture of these solvents in long, radiating needles, m. p. 133°. J. C. W.

Tryptophol (β-Indolylethyl Alcohol), a New Product of the Fermentation of Amino-acids by Yeast. FELIX EHRLICH (*Ber.*, 1912, **45**, 883—889).—Tryptophan (β-indole α-aminopropionic acid) is fermented by living yeast in a similar manner to other amino-acids (Abstr., 1907, ii, 383; 1911, i, 127) with production of carbon dioxide, ammonia, and an alcohol, *β-indolylethyl alcohol*,

$$C_8H_6N\cdot CH_2\cdot CH_2OH,$$

to which the name *tryptophol* is given.

The reaction is carried out either by growing yeast in a sterile solution of tryptophan containing sugar and nutrient salts, or by fermenting the solution directly with pressed yeast in presence of 10% sugar. The fermented solution is filtered through porcelain and evaporated in a vacuum at 40—50° to a syrup, which is extracted with alcohol, the extract evaporated, and the resulting syrup dissolved in water and warmed with sodium hydroxide. The oil which separates is then dissolved out with ether, and the ethereal solution on evaporation deposits an oil which soon becomes crystalline. After purification the substance separates in colourless, monosymmetric tablets melting at 59°, and subliming unchanged above this temperature. Tryptophol gives the characteristic reactions of an indole derivative. It differs from tryptophan in its reaction to bromine, a white turbidity being produced which on further treatment yields a white or grey, flocculent precipitate.

A delicate test for tryptophol consists in adding to the solution a crystal of dimethylaminobenzaldehyde and sufficient alcohol to dissolve it, and then one drop of 25% hydrochloric acid, when a violet-red coloration is produced, slowly in the cold, rapidly on warming, which is extracted when shaken with amyl alcohol, the alcoholic solution giving an absorption spectrum. One part in 10,000 may be detected in this way.

Tryptophol gives a *benzoate*, $C_{10}H_{10}N\cdot O(COPh)$, pale yellow prisms, melting at 76°, and a *picrate*, brick-red needles, melting at 96°.

Tryptophol is also produced by the fermentation of tryptophan by means of *Willia anomala*. W. J. Y.

Preparation of Isatin-naphthalides, their Homologues and Substitution Products. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 242614).—Isatin methyl ether, $C_6H_4{<}{}^{CO}_{N}{\gg}C\cdot OMe$ (or other oxygen isatin ethers), combines readily with α- or β-naphthylamines to furnish compounds of the following general formula: $C_6H_4{<}{}^{CO}_{NH}{>}C{:}N\cdot C_{10}H_7$ (the isatin nucleus substituted or otherwise).

a-Isatin-a-naphthalide, orange-yellow crystals, m. p. 246°, is prepared at the ordinary temperature in benzene solution; the isomeric *β-naphthalide* forms scarlet-red crystals, and has m. p. 208°.

a-Dibromoisatin-a-naphthalide, brownish-violet crystals, m. p. 223°, and the corresponding *β-naphthalide*, dark blue crystals, m. p. 226°, are also described. F. M. G. M.

Stereoisomerism with Compounds Containing Asymmetric Nitrogen and Active Asymmetric Carbon. II. EDGAR WEDEKIND and F. NEY (*Ber.*, 1912, **45**, 1298—1315. Compare Abstr., 1909, i, 514; also E. and O. Wedekind, Abstr., 1908, i, 258).—An extension of the investigation of compounds of the type

$$C_6H_4{<}{\begin{matrix}CH_2\cdot CH_2\\ —CH_2—\end{matrix}}{>}N{\begin{matrix}\diagup R\\ —I\\ \diagdown CH_2\cdot CO_2\cdot C_{10}H_{19}\end{matrix}}$$

, namely, iodides of *l*-menthyl esters of 2-alkyltetrahydro*iso*quinoliniumacetic acids. Several of these have now been resolved into pairs of stereoisomerides, one stereoisomeride being frequently much less stable than the other. The authors believe that the stable isomerides are those containing the lævo-configuration of the nitrogen atom. No definite case of such isomerism could be detected with compounds in which the tetrahydro*iso*quinoline is replaced by two different alkyl radicles.

2-Methyltetrahydro*iso*quinoline (*iso*kairoline) reacts vigorously with *l*-menthyl iodoacetate, forming the l-*menthyl* ester of 2-*methyltetrahydro*iso-*quinoliniumacetic acid iodide*, a colourless, crystalline powder, $[\alpha]_D$ −32° (approx.) in chloroform, decomp. 130—131°; it could not be resolved by fractional crystallisation. Treatment of the alcoholic solution with silver oxide produces menthol and an inactive *betaine*, colourless crystals, decomp. 137—138°.

iso*Propyl*iso*quinolinium iodide* (yellow needles, decomp. 167—169°) is reduced by tin and hydrochloric acid to 2-iso*propyltetrahydro*iso*quinoline*, b. p. 256—258°/735 mm., which with *l*-menthyl iodoacetate produces the l-*menthyl* ester of 2-iso*propyltetrahydro*iso*quinoliniumacetic acid iodide*; this can be separated by crystallisation into a less soluble form ($[\alpha]_D$ −12·54° in alcohol, decomp. 146—148°) and a more soluble form ($[\alpha]_D$ −40·12° in alcohol, decomp. 161—163°). The first form on evaporation of its alcoholic solution undergoes rearrangement, giving the latter isomeride.

2-*Allyltetrahydro*iso*quinoline* (b. p. 255—256°) was converted into the l-*menthyl* ester of 2-*allyltetrahydro*iso*quinoliniumacetic acid iodide*, a solid (decomp. 138—140°), which crystallises only with difficulty.

n-*Butyl*iso*quinolinium iodide* forms yellow needles, decomp. 109—110°; by reduction it gives 2-n-*butyltetrahydro*iso*quinoline*, an almost colourless oil, b. p. 272—273°. This can be converted into the l-*menthyl* ester of 2-n-*butyltetrahydro*iso*quinoliniumacetic acid iodide*, which on recrystallisation gives pearly scales, $[\alpha]_D$ (in alcohol) −29·2°, decomp. 155—156°, whilst the mother liquor yields an isomeride, $[\alpha]_D$ −18·1°, decomp. 140—141°. The latter isomeride in acetone solution is largely converted into the former. Treatment of an alcoholic solution of the more stable isomeride with silver oxide causes complete racemisation at the nitrogen atom.

2-*iso*Butyltetrahydro*iso*quinoline is difficult to prepare, and the product with *l*-menthyl iodoacetate is a vitreous mass.

iso*Amyl*iso*quinolinium iodide*, yellow needles, decomp. 118°, is reducible to 2-iso*amyltetrahydro*iso*quinoline* (a pale yellow liquid, b. p. 276—280°). The l-*menthyl* ester of 2-iso*amyltetrahydro*iso*quinoliniumacetic acid iodide* can be separated by recrystallisation into two fractions, one having $[\alpha]_D +6\cdot4°$ in alcohol, decomp. 164—165°, the other $[\alpha]_D -26\cdot1°$, decomp. 156—158° (two other fractions decomposing at 184—185° and 152—154° respectively are ascribed to impurity in the *iso*amyl iodide originally taken). The *d*-rotatory specimen on keeping in alcoholic solution suffers rearrangement to the stereoisomeride. When the latter is treated in methyl-alcoholic solution with silver oxide, the resultant solution shows for a time a rapidly decreasing lævo-rotation, indicating auto-racemisation of the resultant *betaine*.

n-*Octyl*iso*quinolinium iodide* (yellow needles, decomp. 83—85°) is reducible to 2-n-*octyltetrahydro*iso*quinoline*, b. p. 205—210°/25 mm.; the l-*menthyl* ester of 2-n-*octyltetrahydro*iso*quinoliniumacetic acid iodide* forms leaflets, decomp. 169—170°. Fractional recrystallisation gives products having the same temperature of decomposition, but with optical activity in alcoholic solution, varying from $[\alpha]_D -21\cdot16°$ to $-14\cdot96°$.

Benzylmethylethylamine (b. p. 194—196°) and benzylmethyl-*n*-propylamine (b. p. 215—217°) give no crystalline product with *l*-menthyl iodoacetate.

Benzylethyl-n-*propylamine* (b. p. 222—225°) gives the l-*menthyl* ester of *benzylethyl*-n-*propylammoniumacetic acid iodide.* Recrystallisation from various solvents only produced indefinite fractions with decomposition temperatures varying between 105° and 122°, and $[\alpha]_D$ varying between $-28°$ and $-45°$.

Benzylethyl-n-*butylamine* (b. p. 238—240°) gives the l-*menthyl* ester of *benzylethyl*-n-*butylammoniumacetic acid iodide*, an apparently single substance, decomp. 131°.

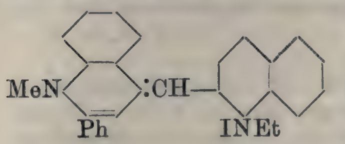
*Benzylethyl*iso*propylamine* (b. p. 212—215°) and *benzylethyl*iso*butylamine* (b. p. 232—234°) when treated with *l*-menthyl iodoacetate both give deposits of benzylethylamine hydriodide (decomp. 126°).

D. F. T.

Quinoline Dyes. II. Constitution, Synthesis, and Degradation of Cyanines. ADOLF KAUFMANN and ERNST VONDERWAHL (*Ber.*, 1912, 45, 1404—1419. Compare Abstr., 1911, i, 328).—It has long been known that the cyanines and *iso*cyanines are diquinolylmethane derivatives, and that the methane carbon atom is attached to one of the quinoline nuclei in position 4 in the cyanines and in position 2 in the *iso*cyanines. The attachment of the methane carbon atom to the other quinoline nucleus has hitherto been undecided. However, since 1 : 2-dimethylquinolinium iodide reacts in the presence of alkali, not only with itself, but with the alkyliodide of any 2-substituted quinoline to form *iso*cyanines, it is certain that in the cyanines and the *iso*cyanines the methane carbon atom is attached to the second quinoline nucleus in position 4. This is so even when the nucleus in question contains an easily mobile

substituent in position 4; thus, whilst 1:2-dimethylquinolinium iodide and 4-phenyl-2-methyl-1-ethylquinolinium iodide do not yield an *iso*cyanine, 2-methyl-1-ethylquinolinium iodide reacts with 4-chloro-1-ethylquinolinium iodide to form ethyl-red, and with 4-*chloro-2-phenyl-1-methylquinolinium iodide*, m. p. 163—164°, to form the same dye as it does with 2-phenyl-1-methylquinolinium iodide (compare König, Abstr., 1906, i, 207).

The last-mentioned dye is 2-*phenyl*-1-*methylquinolylene*-4(2′)-*quinaldine ethiodide*, m. p. 232—233°, green needles (the yellow normal *iodide*, $C_{28}H_{26}N_2I_2,H_2O$, has m. p. about 189°), and receives the annexed formula, because it loses ethyl iodide by heating and yields 2-*phenyl*-1-*methylquinolylene*-4(2′)-*quinaldine*, m. p. 177°, brownish-yellow leaflets and needles, which in boiling alcoholic solution is oxidised by 1% potassium permanganate to 2-phenyl-1-methyl-4-quinolone, quinaldic acid, and another (unidentified) acid, m. p. about 198°.



2-*Methyl*-1-*ethylquinolylene*-4(2′)-*quinaldine ethiodide*,

$$NEt<\genfrac{}{}{0pt}{}{-C_6H_4-}{CMe:CH}>C:CH\cdot C<\genfrac{}{}{0pt}{}{CH:CH}{NEtI-}>C_6H_4,$$

m. p. 183°, dichroic, monoclinic crystals, prepared from 2-methyl-1-ethylquinolinium iodide and 10% potassium hydroxide in boiling methyl alcohol, forms a *periodide*, m. p. 160—162°, reddish-violet needles, which forms a normal *iodide*, $C_{24}H_{26}N_2I_4$, m. p. 196°.

Diethylerythro*apo*cyanine (*loc. cit.*) is obtained as a by-product in the preparation of ethyl-red from the ethiodides of quinoline and quinaldine and 10% alcoholic potassium hydroxide at the ordinary temperature. When the preparation is effected at the b. p., more ethyl-red and less of the *apo*cyanine dye are produced, whilst quinoline, 1-ethyltetrahydroquinoline, and unchanged quinaldine ethiodide have also been isolated from the products of the reaction.

Ethyl-red [1-ethylquinolylene-4(2′)-quinaldine ethiodide] possesses the property of forming alcoholates, any one of which can be changed to another by long keeping or by short heating with an excess of the alcohol in question; thus the *methanol*, $C_{23}H_{23}N_2I,MeOH$, dichroic prisms or plates, and the *ethanol*, $C_{23}H_{23}N_2I,EtOH$, green, dichroic needles, obtained from ethyl-red and the respective alcohols, are converted by hot amyl alcohol into the *pentanol*,

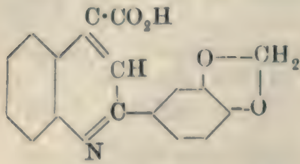
$$C_{23}H_{23}N_2I,C_5H_{11}\cdot OH,$$

small, dichroic crystals.

The monoacidic salts of ethyl-red are intensely coloured; the di-acidic salts, for example, the *hydriodide*, $C_{23}H_{23}N_2I,HI,H_2O$, m. p. 233—234°, are yellow and unstable. C. S.

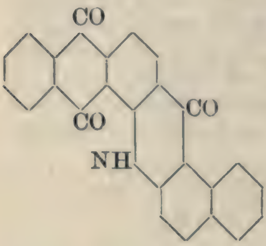
Preparation of 2-Piperonylquinoline-4-carboxylic Acid (Piperonylcinchonic Acid). Chemische Fabrik auf Actien vorm. E. Schering (D.R.-P. 244497).—2-Phenylquinoline-4-carb-

oxylic acid (phenylcinchonic acid) is of therapeutic value but, possesses an unpleasant taste, a disadvantage from which the corresponding piperonyl derivative is free.



2-*Piperonylquinoline*-4-*carboxylic acid* (annexed formula), a green or grey, crystalline powder, m. p. 215°, is prepared by the condensation of aniline (93 parts), piperonal (150 parts), and pyruvic acid (88 parts) in hot alcoholic solution; the product separates on cooling.

F. M. G. M.



[Preparation of Naphthanthracridone.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 242063). — *Naphthanthracridone* (annexed formula), prepared by the condensation of 1-naphthylaminoanthraquinone-2-carboxylic acid, is readily halogenated, yielding orange-brown or red compounds these furnish valuable vat dyes.

F. M. G. M.

Preparation of a Condensation Product from Dihydro-1 : 4-benzothiazone. ACTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 243196. Compare Abstr., 1897, i, 302; 1898, i, 96).—When the colourless ketodihydro-1 : 4-benzothiazine is heated at 210—220° or boiled with nitrobenzene, naphthalene, or other indifferent solvents, it yields a red, crystalline condensation *product*, m. p. 358° (decomp.).

F. M. G. M.

Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXVI. Action of Chlorine on Benzaldazine and Benzoylbenzylidenehydrazide. ROBERT STOLLÉ (*J. pr. Chem.*, 1912, [ii], 85, 386—390. Compare Abstr., 1909, i, 123).—When dissolved in carbon tetrachloride and treated with chlorine at the ordinary temperature, benzaldazine is converted into dibenzoylhydrazide dichloride, CPhCl:N·N:CPhCl (Abstr., 1906, i, 461), which reacts with magnesium phenyl bromide in ethereal solution, yielding diphenylketazine; chlorination at the b. p. of carbon tetrachloride results in the formation of benzonitrile and *benzoylbenzylidenehydrazide chloride*, CHPh:N·N:CPhCl, which crystallises in colourless prisms, m. p. 56°, yields benzoylbenzylidenehydrazide with alcoholic silver nitrate or aqueous sodium carbonate, and on further treatment with chlorine is transformed into benzonitrile.

Chlorine reacts with benzoylbenzylidenehydrazide in ice-cold carbon tetrachloride solution, yielding 2 : 5-diphenyl-1 : 3 : 4-oxadiazole; in hot solution, benzoyl chloride and benzylidene dichloride, together with a small amount of the oxadiazole, are produced.

A solution of benzoylbenzylidenehydrazide and iodine in carbon tetrachloride, on treatment with chlorine at the ordinary temperature, deposits a yellow substance, m. p. 128°, which is converted by crystal-

lisation from the same solvent into 2:5-*diphenyl*-1:3:4-*oxadiazole chloroiodide*, $C_{14}H_{10}ON_2ClI$. This crystallises in yellow leaflets or prisms, m. p. 151°, liberates iodine from potassium iodide, and has also been obtained by the action of chlorine on 2:5-diphenyl-1:3:4-oxadiazole in the presence of iodine.

The interaction of chlorine and benzylideneaniline in carbon tetrachloride solution yields benzylidene-*p*-chloroaniline hydrochloride.

When kept for several months over potassium hydroxide, benzaldazine tetrabromide loses half its bromine, and yields a yellowish-red product, which is converted by sodium carbonate into benzaldazine and benzylideneaminodiphenylpyrrodiazole (Abstr., 1905, i, 249).

Benzaldazine hydrobromide, $C_{14}H_{12}N_2,HBr$, prepared from its components in ethereal solution, forms small, pale yellow leaflets, m. p. 165°.

2:5-*Diphenyl*-1:3:4-*oxadiazole hydrobromide*, $C_{14}H_{10}ON_2,HBr$, is a white powder, m. p. 200°. F. B.

Reduction of Aromatic Aldazines. THEODOR CURTIUS (*J. pr. Chem.*, 1912, 85, [ii], 393—484).—A continuation of previous work (this vol., i, 137, 307).

[With GUSTAV KÜPPERS.]—s-*Di*-o-*hydroxybenzylhydrazine*,

$$N_2H_2(CH_2\cdot C_6H_4\cdot OH)_2,$$

prepared by reducing di-*o*-hydroxybenzaldazine (salicaldazine) with sodium amalgam in alcoholic solution and decomposing the resulting *disodium* salt, $N_2H_2(CH_2\cdot C_6H_4\cdot ONa)_2$, with carbon dioxide, crystallises in white leaflets, m. p. 117°, is not hydrolysed by boiling with hydrochloric acid, and differs from the previously-described derivatives of *s*-dibenzylhydrazine, which form only monohydrochlorides, in yielding a *dihydrochloride*, crystallising in slender, white needles, m. p. 143°; the *diacetyl* derivative, $N_2Ac_2(CH_2\cdot C_6H_4\cdot OAc)_2$, crystallises in white leaflets, m. p. 178—179°; the *tetra-acetyl* derivative,

$$N_2Ac_2(CH_2\cdot C_6H_4\cdot OH)_2,$$

has m. p. 107°. When treated with sodium nitrite, its solution in dilute acetic acid deposits a yellowish-brown, crystalline *dinitroso*-compound, $N_2(NO)_2(CH_2\cdot C_6H_4\cdot OH)_2$, which becomes brown at 80°, m. p. 90° (decomp.), gives off nitrous acid on exposure to air, and when boiled in alcoholic solution is converted into o-*hydroxybenzaldehydenitroso*-o-*hydroxybenzylhydrazone*,

$$OH\cdot C_6H_4\cdot CH{:}N\cdot N(NO)\cdot CH_2\cdot C_6H_4\cdot OH.$$

This crystallises in slender, pale bronze-yellow needles, m. p. 145°, and is hydrolysed by strong hydrochloric acid to salicylaldehyde.

s-*Di*-m-*hydroxybenzylhydrazine*, prepared by reducing di-*m*-hydroxybenzaldazine with sodium amalgam and alcohol, crystallises in pale yellow needles, m. p. 183°, and resembles the preceding ortho-compound in forming a *diacetyl* derivative, m. p. 209°, *tetra-acetyl* derivative, m. p. 132°, and *dihydrochloride*, m. p. 154°. Attempts to prepare a dihydrotetrazone by boiling an alcoholic solution of the hydrazine with mercuric oxide gave *m*-hydroxybenzaldehyde. On treatment with nitrous acid it yields m-*hydroxybenzaldehydenitroso*-m-*hydroxybenzylhydrazone*, which crystallises in slender, white needles, m. p. 112—114° (decomp.).

[With RUDOLF GLASER.]—The *disodium* salt of di-*o*-hydroxybenzaldazine, $N_2(CH\cdot C_6H_4\cdot ONa)_2$, prepared by the addition of alcoholic sodium ethoxide to a suspension of the aldazine in aqueous alcohol, forms greenish-yellow, rectangular, anisotropic plates, which become deep red at 180°, and char at a higher temperature without melting. It is decomposed by water with the separation of the original aldazine.

Di-*o*-ethoxybenzaldazine (Pascal and Normand, this vol., i, 147), obtained by heating di-*o*-hydroxybenzaldazine with sodium ethoxide and ethyl iodide in alcoholic solution, forms a *hydrochloride*,

$$C_{18}H_{20}O_2N_2,HCl,$$

m. p. 146°, which is resolved into its components by dissolving in alcohol.

Di-*o*-methoxybenaldazine (Bouveault, Abstr., 1899, i, 287), prepared in a similar manner, yields a reddish-yellow, crystalline *hydrochloride*, m. p. 160°.

Di-*o*-benzyloxybenzaldazine, from salicaldazine and benzyl chloride, has m. p. 150° (Pascal and Normand, *loc. cit.*, give 157·7°), and resembles the preceding methoxy- and ethoxy-compounds in being readily hydrolysed by sulphuric acid.

Di-*o*-ethoxybenzaldazine is reduced by zinc dust and acetic acid in alcoholic solution to *di-o-ethoxybenzylamine*, $NH(CH_2\cdot C_6H_4\cdot OEt)_2$. This is a pale yellow oil, b. p. 180°/20 mm., and yields a *hydrochloride*, *nitrate*, *picrate*, and *platinichloride*, but only the last-mentioned salt could be obtained in the solid condition.

Di-o-methoxybenzylamine, $C_{16}H_{19}O_2N$, prepared from di-*o*-methoxybenzaldazine in a similar manner, has b. p. 200°/30 mm.; of its salts only the *platinichloride* is solid.

[With GEORG DETOROS.]—Di-*o*-methoxybenzaldazine is reduced by sodium amalgam and alcohol to o-*methoxybenzaldehyde*-o-*methoxybenzylhydrazone*, $OMe\cdot C_6H_4\cdot CH:N\cdot NH\cdot CH_2\cdot C_6H_4\cdot OMe$, which forms white needles of a silky lustre, m. p. 76°, and yields an *acetyl* derivative, crystallising in lustrous prisms, m. p. 101°; the *benzoyl* derivative has m. p. 170°.

The *nitroso*-derivative, $OMe\cdot C_6H_4\cdot CH:N\cdot N(NO)\cdot CH_2\cdot C_6H_4\cdot OMe$, forms pale yellow needles, m. p. 91°.

s-*Di*-o-*methoxybenzylhydrazine*, $N_2H_2(CH_2\cdot C_6H_4\cdot OMe)_2$, obtained by reducing di-*o*-methoxybenzaldazine with alcohol and excess of sodium amalgam, and isolated in the form of its *hydrochloride* (long, yellow needles, m. p. 154°), yields a *diacetyl* derivative, m. p. 133—134°. Attempts to prepare the corresponding dibenzoyl and dinitroso-derivatives resulted in the formation of the above-mentioned benzoyl and nitroso-derivatives of *o*-methoxybenzaldehyde-*o*-methoxybenzylhydrazone.

o-*Methoxybenzylhydrazine*, $OMe\cdot C_6H_4\cdot CH_2\cdot NH\cdot NH_2$, obtained in the form of its *hydrochloride* (lustrous, white needles, m. p. 123—124°) by hydrolysing *o*-methoxybenzaldehyde-*o*-methoxybenzylhydrazone with dilute hydrochloric acid, is a colourless liquid, b. p. 145—149°/14 mm., and condenses with ethyl acetoacetate, forming 1-o-*methoxybenzyl*-3-*methyl*-5-*pyrazolone*, $\begin{matrix} CH_2\cdot CO \\ | \\ CMe{=}N \end{matrix}\!\!>\!N\cdot CH_2\cdot C_6H_4\cdot OMe$, which crys-

tallises in rosettes of red needles, m. p. 82—84°. Its hydrochloride reacts with pyruvic acid in concentrated aqueous solution, yielding *α-o-methoxybenzylhydrazonopropionic acid*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot NH\cdot N\colon CMe\cdot CO_2H,$$

lustrous prisms, m. p. 107·5°, and with potassium cyanate to form *o-methoxybenzylsemicarbazide*, $OMe\cdot C_6H_4\cdot CH_2\cdot N(NH_2)\cdot CO\cdot NH_2$, m. p. 214—215°.

The *nitroso*-derivative, $OMe\cdot C_6H_4\cdot CH_2\cdot N(NO)\cdot NH_2$, crystallises in lustrous, white needles, m. p. 65°, condenses with *o*-methoxybenzaldehyde, yielding the corresponding nitroso-*o*-methoxybenzylhydrazone, and when boiled with 10% sulphuric acid is converted into *o-methoxybenzylazoimide*, $OMe\cdot C_6H_4\cdot CH_2\cdot N_3$, a colourless liquid, b. p. 118°/14 mm., which is stable toward sodium hydroxide, but is hydrolysed by 30% sulphuric acid with the formation of hydrazoic acid.

o-Methoxybenzaldehyde-o-hydroxybenzylhydrazone,

$$OMe\cdot C_6H_4\cdot CH\colon N\cdot NH\cdot CH_2\cdot C_6H_4\cdot OH,$$

is obtained as a by-product in the reduction of di-*o*-methoxybenzaldazine to *o*-methoxybenzaldehyde-*o*-methoxybenzylhydrazone by sodium amalgam in aqueous alcoholic solution. It forms a white, crystalline powder, which becomes yellow at 115°, has m. p. 153—157°, and is insoluble in the common solvents. The position of the methoxy-group has been established by the formation of *o*-methoxybenzaldehyde on hydrolysis with hydrochloric acid. It forms a *nitroso*-derivative, m. p. 148° (decomp.).

[With Ley Francis Potter.]—*m*-Methoxybenzaldehyde is most conveniently prepared by methylating *m*-hydroxybenzaldehyde with methyl sulphate and aqueous potassium hydroxide. With hydrazine sulphate it yields *di-m-methoxybenzaldazine*, which forms lustrous, yellow leaflets, m. p. 75°, and is different from the compound, m. p. 152°, described under the same name by Bouveault (*loc. cit.*).

s-Di-m-methoxybenzylhydrazine, prepared by reducing the preceding azine with sodium amalgam and alcohol, is a pale yellow oil; the *hydrochloride* forms slender, lustrous, white needles, m. p. 115°, and reacts with sodium nitrite, yielding *m-methoxybenzaldehydenitroso-m-methoxybenzylhydrazone*, yellow needles, m. p. 80° (decomp.), together with a *substance*, m. p. 164°, which crystallises in very light needles resembling down.

m-Methoxybenzylhydrazine is prepared by reducing *s*-di-*m*-methoxybenzaldazine with sodium amalgam and alcohol to *m-methoxybenzaldehyde-m-methoxybenzylhydrazone*, a brownish-yellow oil, and hydrolysing the latter with dilute hydrochloric acid. It forms a colourless oil, b. p. 158—160°/19 mm., which rapidly loses nitrogen when kept; the *hydrochloride* crystallises in stellar aggregates of needles, m. p. 123°, or in transparent plates of triclinic habit, and reacts with pyruvic acid, yielding *α-m-methoxybenzylhydrazonopropionic acid*, which forms fern-like aggregates of needles or rhombic plates, m. p. 99°. The *benzoyl* derivative, $N_2HBz\cdot CH_2\cdot C_6H_4\cdot OMe$, forms needles, m. p. 99°. The *nitroso*-compound, $OMe\cdot C_6H_4\cdot CH_2\cdot N(NO)\cdot NH_2$, crystallises in felted needles, m. p. 45—47°, condenses with *m*-methoxybenzaldehyde to form the previously-described *m*-methoxybenzaldehydenitroso-*m*-methoxybenzylhydrazone, and is converted by distillation with 10%

sulphuric acid into m-*methoxybenzylazoimide*, a colourless liquid, b. p. 134°/28 mm., which differs from the ortho- and para-isomerides in not being hydrolysed by sulphuric acid to hydrazoic acid.

Di-m-*methoxybenzylamine*, $NH(CH_2 \cdot CH_4 \cdot OMe)_2$, prepared by reducing di-*m*-methoxybenzaldazine with zinc dust and acetic acid in alcoholic solution, is an almost colourless liquid, b. p. 225°/13 mm., and forms a *hydrochloride*, white leaflets, m. p. 141°, *nitrate*, needles, m. p. 128°, *picrate*, yellow platelets, m. p. 124°, and a stable *nitrite*, m. p. 104°. It is accompanied by m-*methoxybenzylamine*, $OMe \cdot C_6H_4 \cdot CH_2 \cdot NH_2$, which forms a colourless oil, and yields a *hydrochloride*, crystallising in transparent plates or needles, m. p 160°.

[With KARL TRAUMANN.]—Anisaldazine is reduced by sodium amalgam and alcohol to p-*methoxybenzaldehyde*-p-*methoxybenzylhydrazone*. This crystallises in white leaflets of a silvery lustre, m. p. 143° (decomp.), and yields an *acetyl* derivative, white needles, 87°, *benzoyl* derivative, lustrous, silky needles, m. p. 111—112°, a *nitroso*-compound, $OMe \cdot C_6H_4 \cdot CH{:}N \cdot N(NO) \cdot CH_2 \cdot C_6H_4 \cdot OMe$, crystallising in light yellow leaflets, m. p. 106°, and a *picrate*, m. p. 90° (decomp.).

p-*Methoxybenzylhydrazine hydrochloride*, white needles, m. p. 194—195° (decomp.), is obtained by hydrolysing the preceding hydrazone with hydrochloric acid. On treatment with sodium hydroxide, it yields an oil, which after distillation under diminished pressure yields p-*methoxybenzylhydrazine*, together with the original hydrazone. With pyruvic acid it condenses to form α-p-*methoxybenzylhydrazonopropionic acid*, white needles, m. p. 123—124°. The *dibenzoyl* derivative crystallises in stout, colourless prisms, m. p. 149°; the *nitroso*-derivative in large, lustrous, white plates, m. p. 91°, and is converted by distillation with 10% sulphuric acid into p-*methoxybenzylazoimide*, a colourless, oily liquid, b. p. 126°/14 mm.

s-*Di*-p-*methoxybenzylhydrazine* is obtained by reducing anisaldazine in alcoholic solution with excess of sodium amalgam. It crytallises in colourless leaflets of a silvery lustre, m. p. 71°, and yields a stable *nitrite*, white needles, m. p. 92° (decomp.), which on further treatment with nitrous acid is transformed into *p*-methoxybenzaldehyde-nitroso-*p*-methoxybenzylhydrazone; the *hydrochloride* forms leaflets, m. p. 236—237° (decomp.); the *acetyl* derivatives, lustrous, white, intergrown platelets, m. p. 113°.

When reduced with zinc and acetic acid in alcoholic solution, anisaldazine yields di-*p*-methoxybenzylamine (di-anisylamine), of which the hydrochloride, m. p. 245° (decomp.), nitrate, m. p. 171° (decomp.), and *nitrite*, m. p. 147° (decomp.), are described (compare Steinhart, Abstr., 1888, 51).

[With LEO FRANK GUTTMANN.]—*Piperonaldazine monohydrochloride* separates from a solution of the azine in concentrated hydrochloric acid in dark yellow leaflets, m. p. 207°; the *dihydrochloride*, prepared from its components in chloroform solution, has m. p. 213°, and readily loses hydrogen chloride; the *sulphate*, $C_{16}H_{12}O_4N_2,H_2SO_4$, has m. p. 214 or 221° (decomp.). The *tetrabromide*,

$$N_2Br_2(CHBr \cdot C_6H_3{:}O_2{:}CH_2)_2,$$

forms a red powder, m. p. 185° (decomp.), which when shaken with pure dry acetone yields bromoacetone and *piperonaldazine dihydro-*

bromide, a yellow, crystalline powder. The *monohydrobromide* is obtained by incompletely brominating piperonaldazine and shaking the product with ordinary acetone; it is a yellow, crystalline powder, m. p. 216°. The hydrochlorides and hydrobromides described above are resolved by water into their components.

Piperonaldehydepiperonylhydrazone,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}N{\cdot}NH{\cdot}CH_2{\cdot}C_6H_3{:}O_2{:}CH_2,$$

prepared by reducing the azine with sodium amalgam and alcohol, forms fan-like aggregates of white needles or leaflets, m. p. 116° (decomp.) with previous sintering at 109°; the *nitroso*-derivative crystallises in light yellow needles, m. p. 145° (decomp.), the *acetyl* derivative in small, flat plates, m. p. 146°, the *benzoyl* derivative in tufts of very slender needles, m. p. 125°. It is hydrolysed by dilute hydrochloric acid to *piperonylhydrazine*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}NH{\cdot}NH_2$, which was isolated in the form of its *hydrochloride*, slender, white needles, m. p. 173·5°. The *acetyl* derivative of piperonylhydrazine is an oil; the *picrate*, $C_{14}H_{13}O_9N_5$, m. p. 140·5—141° (decomp.), is reddish-yellow, and crystallises from alcohol in clusters of yellow needles, m. p. 138·5°, containing one molecule of the solvent, which is lost at 98°. A mixture of the mono- and di-benzoyl derivatives is produced by shaking the hydrochloride with benzoyl chloride and aqueous sodium hydroxide.

Piperonylsemicarbazide, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}N(NH_2){\cdot}CO{\cdot}NH_2$, obtained from piperonylhydrazine hydrochloride and potassium cyanate in aqueous solution, forms snow-white needles, m. p. 175°.

Piperonylphenylthiosemicarbazide,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}N(NH_2){\cdot}CS{\cdot}NHPh,$$

from phenylthiocarbimide, crystallises in needles, m. p. 153·5°.

a-Nitroso-a-piperonylhydrazine forms long, slender needles, m. p. 91°, condenses with piperonaldehyde, yielding piperonaldehydenitroso-piperonylhydrazone, and when heated with dilute sulphuric acid is converted into *piperonylazoimide*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}N_3$. The latter compound is a pale yellow oil, b. p. 142°/15 mm., which is decomposed by 30% sulphuric acid into nitrogen, formaldehyde, hydrazoic acid, piperonaldehyde, ammonia, and a solid base, consisting probably of 3 : 4-methylenedioxyaniline (Rupe and Majewski, Abstr., 1901, i, 103).

[With Josef Schmittmann.]—*Piperonylhydrazine* is a pale yellow, viscid oil, b. p. 175—180°/14 mm. It reacts with ethyl acetoacetate, yielding 1-*piperonyl*-3-*methyl*-5-*pyrazolone*,

$$\begin{matrix} CMe{=}N \\ | \\ CH_2{\cdot}CO \end{matrix}\!\!>\!N{\cdot}CH_2{\cdot}C_6H_3{:}O_2{:}CH_2,$$

which crystallises in small needles, m. p. 155°, forms a white *silver* salt, and when dissolved in acetic acid and treated with sodium nitrite is converted into 4-*oximino*-1-*piperonyl*-3-*methyl*-5-*pyrazolone*, $C_{12}H_{11}O_4N_3$. This crystallises in light yellow, microcrystalline needles, m. p. 161°, and forms a greenish-yellow *silver* salt.

3-*Phenyl*-1-*piperonyl*-5-*pyrazolone*, $C_{17}H_{14}O_3N_2$, prepared from piperonylhydrazine and ethyl benzoylacetate, has m. p. 144·5°, and yields a white *silver* salt.

4-*Oximino-3-phenyl-1-piperonyl-5-pyrazolone*, $C_{17}H_{13}O_4N_3$, forms an intensely red powder, m. p. 162° (decomp.); the *silver* salt is yellow.

1-*Piperonyl-3-methyl-6-pyridazinone*,

$$CH_2<\begin{matrix}CH_2\cdot CO\\ CMe{=}N\end{matrix}>N\cdot CH_2\cdot C_6H_3{:}O_2{:}CH_2,$$

prepared by heating piperonylhydrazine with ethyl lævulate, crystallises in long, colourless needles, m. p. 101°. *a-Piperonylhydrazonopropionic acid*, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot NH\cdot N{:}CMe\cdot CO_2H$, obtained from pyruvic acid, forms lustrous, colourless leaflets, m. p. 143°. When reduced with excess of sodium amalgam and alcohol, piperonaldazine yields s-*dipiperonylhydrazine*, $N_2H_2(CH_2\cdot C_6H_3{:}O_2{:}CH_2)_2$, which crystallises in yellow leaflets, m. p. 88°, and when heated in alcoholic solution with mercuric oxide is converted into piperonaldehydepiperonylhydrazone. The hydrazine forms a *hydrochloride*, m. p. 223°, a *diacetyl* derivative, m. p. 138°, *dibenzoyl* derivative, crystallising in yellow leaflets, m. p. 98°, and a *dinitroso*-derivative, which crystallises in white leaflets, m. p. 95° (decomp.), and when warmed in alcoholic solution yields piperonaldehydenitrosopiperonylhydrazone.

[With HERMANN PAULI.]—*Di-o-chlorobenzaldazine tetrabromide*,

$$N_2Br_2(CHBr\cdot C_6H_4Cl)_2,$$

prepared from its components in carbon tetrachloride solution, is an amorphous, red substance, m. p. 172—175° (decomp.).

[With ERNST BOETZELEN.]—*a*-Naphthaldazine has m. p. 156°, and yields a *tetrabromide*, which crystallises in lustrous, golden-yellow, asbestos-like needles, m. p. 170—172°, and is converted by acetone into *a-naphthaldazine dihydrobromide*, $C_{22}H_{16}N_2,2HBr$, bromoacetone being produced simultaneously.

[With ERNST HAAGER.]—It has been shown by Pascal and Normand (this vol., i, 147) that aromatic aldazines are decomposed by heat, giving stilbenes, and that the yield of the latter diminishes as the molecular weight of the azine increases.

This conclusion has been confirmed from the behaviour of di-2:4-dimethylbenzaldazine, which decomposes when heated at 260—370°, yielding considerable quantities of ψ-cumene, 2:4-dimethylbenzonitrile, and ammonia, but only a very small amount of tetramethylstilbene.

F. B.

Quinazolines. XXXI. Action of Methyl and Ethyl Iodides on Dihydro-4-quinazolones. MARSTON T. BOGERT and GEORGE A. GEIGER (*J. Amer. Chem. Soc.*, 1912, 34, 683—693).—In continuation of work on the 4-dihydroquinazolones (this vol., i, 393, 395, and earlier abstracts), a study has been made of their behaviour towards methyl and ethyl iodides, and the following results have been obtained.

4-Dihydroquinazolones do not combine readily with alkyl iodides except under pressure and at temperatures of 110° or more. The iodide attaches itself to the nitrogen atom in the 1-position and not to that in the 3-position. The ethiodides usually have lower m. p.'s, and are more soluble in water or methyl alcohol than the corresponding methiodides. 6-Nitro-4-dihydroquinazolones cannot generally be made to unite with methyl or ethyl iodide. The alkyl iodide

additive products usually have high m. p.'s, and when heated further evolve the alkyl iodide.

By the action of methyl iodide on 4-dihydroquinazolone, 3-methyl-3 : 4-dihydroquinazolone, or 4-methoxyquinazoline, the same product, 3-methyl-3 : 4-dihydroquinazolone methiodide, $C_6H_4{<}\begin{matrix}NMeI{:}CH \\ CO{-}{-}NMe\end{matrix}$, m. p. 274° (corr.), is obtained in each case; this compound was first prepared by Knape (Abstr., 1891, 909). Ethyl iodide reacts with 4-methoxyquinazoline to form a *substance*, m. p. 249° (uncorr.), which has not yet been identified.

The following additive compounds are described: 2-*Methyl*-4-*dihydroquinazolone methiodide*, m. p. 220° (uncorr.); 3-*methyl*-4-*dihydroquinazolone ethiodide*, m. p. 230° (decomp.); 2 : 3-*dimethyl*-4-*dihydroquinazolone methiodide*, m. p. 245° (corr.), and *ethiodide*, m. p. 242° (corr.); 3-*ethyl*-4-*dihydroquinazolone methiodide*, m. p. 258° (decomp.), and *ethiodide*, m. p. 181° (corr.); 2-*methyl*-3-*ethyl*-4-*dihydroquinazolone methiodide*, m. p. 220° (decomp.), and *ethiodide*, m. p. 177° (corr.); 3-*benzyl*-4-*dihydroquinazolone methiodide*, m. p. 188° (corr.); 3-*phenyl*-2-*methyl*-4-*dihydroquinazolone methiodide*, m. p. 243° (decomp.), and *ethiodide*, m. p. 244° (corr.). 3-p-*Tolyl*-2-*methyl*-4-*dihydroquinazolone methiodide* has m. p. 234·5° (decomp.), and the *methiodides* of 3-*p*-anisyl-, 3-*p*-phenetyl-, 3-α- and 3-β-naphthyl-2-methyl-4-dihydroquinazolone melt and decompose at 231·5°, 221°, 235°, and 238° respectively.

Attempts to methylate the amino-group of 3-amino-2-methyl-4-dihydroquinazolone with methyl iodide or sulphate in presence of alkali hydroxide were not successful, but by the action of methyl iodide alone, a *methiodide*, m. p. 201° (decomp.), was obtained.

2-Styryl-4-dihydroquinazolones add methyl iodide more easily than ethyl iodide. 3-Phenyl-, 3-*p*-anisyl-, 3-*p*-phenetyl-, and 3-α-naphthyl-2-styryl-4-dihydroquinazolones do not unite with methyl iodide when heated with it for ten hours at 150°. 2-*Styryl*-4-*dihydroquinazolone methiodide* has m. p. 235° (corr.), and when treated with silver nitrate is converted into the corresponding *methyl nitrate* compound, m. p. 177° (decomp.). 2-*Styryl*-4-*dihydroquinazolone ethiodide* has m. p. 217—218° (uncorr.); 2-*styryl*-3-*methyl*-4-*dihydroquinazolone methiodide*, m. p. 214° (decomp.); 2-*styryl*-3-*ethyl*-4-*dihydroquinazolone methiodide*, m. p. 207·5° (uncorr.); 3-p-*tolyl*-2-*styryl*-4-*dihydroquinazolone*, m. p. 219·5° (decomp.); 6-*nitro*-3-*methyl*-4-*dihydroquinazolone methiodide*, m. p. 228·5° (corr.); 2-*phenylbutadienyl*-4-*dihydroquinazolone methiodide*, m. p. 232·5° (corr.); and 2-p-*hydroxy*-m-*methoxystyryl*-4-*dihydroquinazolone methiodide*, m. p. 223—225° (uncorr.). E. G.

Benzoylcyanamide and a Synthesis of Benzoylenecarbamide (Diketotetrahydroquinazoline) from *o*-Nitrobenzoylcyanamide. OTTO DIELS and ALFRED WAGNER (*Ber*, 1912, **45**, 874—883).—Benzoylcyanamide is easily prepared by shaking cyanamide with benzoyl chloride and sodium hydroxide; it has m. p. 141—142° (corr.). By the action of chlorine on it, chlorobenzoylcarbamide (Chattaway and Wünsch, Trans, 1909, **95**, 129) is obtained. When this is treated in

the cold with dilute sodium hydroxide, hydrogen chloride is eliminated and a well characterised *compound*, $C_8H_6O_2N_2$, is obtained crystallising in platelets or needles, m. p. 141°, which perhaps has the constitution $COPh{\cdot}N{<}\begin{smallmatrix}CO\\ |\\ NH\end{smallmatrix}$. It unites with phenylcarbimide to form a *compound*, $C_{15}H_{11}O_3N_3$, m. p. 150°.

as-*Di-o-nitrodibenzoylcarbamide*, $NH_2{\cdot}CO{\cdot}N(CO{\cdot}C_6H_4{\cdot}NO_2)_2$, from cyanamide, pyridine, and *o*-nitrobenzoyl chloride, crystallises in rods and rectangular platelets, m. p. 200° (corr.). On oxidation with hydrogen peroxide in alkaline solution, one acyl group is eliminated and o-*nitrobenzylcarbamide* obtained. This is more conveniently prepared by the action of *o*-nitrobenzoyl chloride on carbamide; it crystallises in well formed yellow needles, m. p. 237° (corr., decomp.).

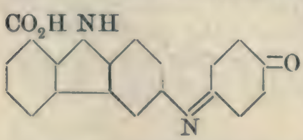
On reduction, o-*aminobenzoylcarbamide*, $NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, is obtained; it crystallises in small, brown needles, which on heating at 200° are converted quantitatively into *diketotetrahydroquinazoline*, $C_6H_4{<}\begin{smallmatrix}CO-NH\\ \ \ \ \ \ \ \ |\\ NH{\cdot}CO\end{smallmatrix}$. This separates in beautiful colourless crystals, m. p. 356° (corr.). Its solutions in concentrated sulphuric acid and in dilute alkalis fluoresce with a bluish-violet ground tone. E. F. A.

Preparation of Nitrated Derivatives of Indigotin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 242149).—Nitro-derivatives of indigotin are readily prepared by nitrating indigotin in the complete absence of water. Indigotin (13 parts) is added to a mixture of concentrated sulphuric acid (50 parts) with fuming acid (100 parts), and 6·3 parts of nitric acid (100%) mixed with concentrated sulphuric acid slowly dropped in at a temperature of −5° to −10°. The *nitroindigotin* prepared under these conditions forms a glistening, brown powder, and by increasing the proportion of nitric acid more highly nitrated indigotins are obtained.

The nitration of 2 : 1-naphthylindigotin, 5 : 5′-dibromoindigotin, dehydroindigotin acetate, and 5 : 5′-dibromodehydroindigotin acetate is also considered in the original, and the products are stated to reduce readily to the corresponding primary diazotisable amines.

F. M. G. M.

Preparation of Indophenol Condensation Products and their Leuco-derivatives from Carbazolecarboxylic Acids. LEOPOLD CASSELLA & Co. (D.R.-P. 241899. Compare Abstr., 1911, i, 488).—When carbazolecarboxylic acid is condensed with *p*-nitrosophenol in concentrated sulphuric acid solution, a *product* (annexed formula) is obtained in the form of a blue powder.



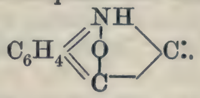
Ethyl carbazolecarboxylate crystallises from ether in glistening prisms, and forms a *product* with *p*-nitrosophenol. F. M. G. M.

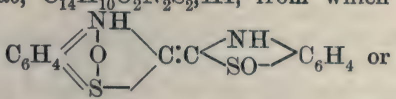
Preparation of Indophenol Condensation Products from Perimidine and its Derivatives. ACTIEN GESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 243545).—It is found that perimidine and its derivatives are readily converted into indophenols

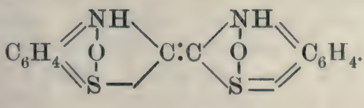
by condensation with aminophenols in the presence of an oxidising agent, or by condensation with *p*-benzoquinonechloroimide.

When 2-methylperimidine (18·2 parts) and 2 : 6-dichloro-*p*-aminophenol hydrochloride (21 parts) are heated at 40° in dilute acetic acid with sodium dichromate, the *product* separates as a dark crystalline powder with a metallic lustre, whilst the *compound* from perimidine and *p*-benzoquinonechloroimide forms a reddish-violet mass. These compounds dissolve in alkali hydroxides with a blue coloration.

F. M. G. M.

"Thionylindigo." M. Claasz (*Ber.*, 1912, 45, 1015—1032).—The suggestion is advanced that the colour of indigotin is due, not to the chromophore, CO·C⁚C·CO, but to an orthoquinonoid configuration, indigotin containing, therefore, the group  In order to test the theory, it is necessary to prepare an "indigo" in which the carbonyl groups are replaced by groups which are not chromophores and yet are capable of tautomeric change. The thionyl group has been selected, because a comparison of the three yellow substances, benzil, anthraquinone, and acridone, with the three colourless substances, diphenyl disulphoxide, cyclic diphenyl disulphoxide, and diphenylamine sulphoxide respectively, shows that the thionyl group is devoid of chromophoric character. Were the colour of indigotin due to the chromophore CO·C⁚C·CO, it is to be expected, therefore, that "thionylindigo," $C_6H_4<{NH \atop SO}>C:C<{NH \atop SO}>C_6H_4$, will be much less intensely coloured. The substance, however, has a deep bluish-black colour. Consequently a quinonoid structure is claimed for indigotin and for "thionylindigo," although it has not been decided whether one or two such groups are present in these molecules.

"Thionylindigo" has been obtained by the fusion of phenylglycine-*o*-sulphinic acid with potassium hydroxide, whilst its synthesis has been effected in the following way. *o*-Aminophenyl mercaptan hydrochloride, disolved in water covered with ether, reacts with 40% formaldehyde to form *benzothiazoline*, $C_6H_4<{NH \atop S}>CH_2$, b. p. 270°, a yellow oil, an ethereal solution of which reacts with 1% iodine in aqueous potassium iodide in the presence of a concentrated solution of sodium hydrogen carbonate to yield "*benzothiazolinesulphine iodide,*" $C_6H_4<{NH \atop SI}\geqslant CH$. The latter is a brown powder, which in glacial acetic acid reacts with hydrogen peroxide to form "*thionylindigo*" *hydriodide*, $C_{14}H_{10}O_2N_2S_2,HI$, from which alkalis liberate "thionylindigo,"  or



This substance yields with alkaline sodium hyposulphite a brown vat, which has very little affinity for the fibre, and is not re-oxidised by air, but is re-converted into "thionylindigo" by dilute hydrogen peroxide.

The following compounds have been obtained in the course of experiments to prepare "thionylindigo" by other methods. *o*-Nitrophenyl methyl sulphide yields 4-*bromo-2-nitrophenyl methyl sulphide*,

$$NO_2\cdot C_6H_3Br\cdot SMe,$$

m. p. 130—131°, yellow needles, by bromination in hot acetic acid, and is converted into o-*nitrophenylmethylsulphone*, $NO_2\cdot C_6H_4\cdot SO_2Me$, m. p. 106°, colourless plates, by oxidation in hot glacial acetic acid by hydrogen peroxide. The bromination of *o*-nitrophenylthiolacetic acid in hot glacial acetic acid yields o-*nitrophenyldibromomethylsulphoxide*, $NO_2\cdot C_6H_4\cdot SO\cdot CHBr_2$, m. p. 141°, colourless needles. The sulphoxide is not oxidised by hydrogen peroxide to the corresponding *sulphone*, $NO_2\cdot C_6H_4\cdot SO_2\cdot CHBr_2$, m. p. 138°, colourless prisms, which is obtained, however, by the bromination of *o*-nitrophenylsulphoneacetic acid. *o*-Nitrophenylmethylsulphone is reduced to o-*aminophenylmethylsulphone*, $NH_2\cdot C_6H_4\cdot SO_2Me$, m. p. 85—92°, to o-*azoxyphenylmethylsulphone*, $SO_2Me\cdot C_6H_4\cdot \overset{O}{\overbrace{N\text{——}N}}\cdot C_6H_4\cdot SO_2Me$, m. p. 222°, yellow leaflets, by zinc dust and hot 90% acetic acid, and to o-*hydroxylaminophenylmethylsulphone*, $OH\cdot NH\cdot C_6H_4\cdot SO_2Me$, by zinc dust and 40% acetic acid in the cold; the last substance yields the two preceding by autoreduction and autoxidation. When a boiling alcoholic solution of di-*o*-nitrophenyl disulphide is treated with sodium sulphide and sodium hydroxide and the clear filtrate reacts with ethylene dibromide, o-*nitrophenylsulphuran*, $NO_2\cdot C_6H_4\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot C_6H_4\cdot NO_2$, m. p. 206—208°, yellow crystals, is obtained, which is oxidised in hot glacial acetic acid by hydrogen peroxide to *di*-o-*nitrophenylsulphonylethane*, $C_2H_4(SO_2\cdot C_6H_4\cdot NO_2)_2$, m. p. 258°, colourless needles. The latter is reduced to *di-o-aminophenylsulphonylethane*, m. p. 155—158°, by zinc dust and hot 50% acetic acid.

An alcoholic solution of sodium *o*-nitrophenyl mercaptide reacts with ethyl chloroacetate at 60° to form *ethyl* o-*nitrophenylthiolacetate*,

$$NO_2\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2Et,$$

m. p. 46—48°, brown needles, which in glacial acetic acid is oxidised by hydrogen peroxide to *ethyl* o-*nitrophenylsulphoxidoacetate*,

$$NO_2\cdot C_6H_4\cdot SO\cdot CH_2\cdot CO_2Et,$$

m. p. 75—78°, or to *ethyl* o-*nitrophenylsulphoneacetate*,

$$NO_2\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot CO_2Et,$$

m. p. 55—57°, according to the experimental conditions; the latter is converted into di-*o*-nitrophenyl disulphide by alcoholic ammonium sulphide.

C. S.

Hydrazine Derivatives of Pyridinecarboxylic Acids. HANS MEYER and JOSEF MALLY (*Monatsh.*, 1912, 33, 393—414).—The condensation products of hydrazine hydrate with the esters of the three pyridinemonocarboxylic acids, of dipicolinic, quinolinic and cinchomeronic acids have been investigated. In general, the compounds are readily prepared and are crystalline when pure materials are employed. The use of crude material leads to unsatisfactory results.

Picolinic hydrazide was obtained in colourless needles, m. p. 100°, by warming ethyl picolinate with hydrazine hydrate. It condenses readily with aldehydes; thus *benzylidenepicolinic hydrazide*, m. p. 108°, *vanillylidenepicolinic hydrazide*, m. p. 208—209°, and o-*chlorobenzylidenepicolinic hydrazide*, m. p. 147°, were isolated. When picolinic hydrazide is treated with hydrochloric acid and sodium nitrite, the very volatile *picolinazoimide* is obtained, which passes into the corresponding *urethane*, m. p. 102—103°, when its alcoholic solution is boiled. The latter substance is slowly hydrolysed by boiling fuming hydrochloric acid with the formation of the hydrochloride of 2-aminopyridine, which was identified by means of its platinichloride.

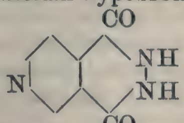
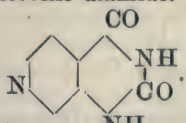
The hydrazide and benzylidenehydrazide of nicotinic acid have been described by Curtius and Mohr (Abstr., 1899, i, 73). o-*Chlorobenzylidenenicotinic hydrazide* has m. p. 160—161°. *Vanillylidenenicotinic hydrazide*, m. p. 126—127°, yields a yellow, crystalline *hydrochloride*, m. p. 241—243° (decomp.).

Ethyl *iso*nicotinate, when similarly treated, yielded iso*nicotinic hydrazide*, m. p. 163°, which combined with two molecules of hydrochloric acid, forming a *hydrochloride*, m. p. above 300°. Poor yields of the volatile *azoimide* were obtained when the hydrazide was acted on by sodium nitrite and hydrochloric acid. *Benzylidene*iso*nicotinic hydrazide*, *vanillylidene*iso*nicotinic hydrazide*, m. p. 218°, and o-*chlorobenzylidene*iso*nicotinic hydrazide*, m. p. 214°, were prepared.

From dipicolinic acid (measurement of the rhombic crystals of which gave $a:b:c=0·7221\ 1:1·2866$), the following series of derivatives was obtained: *dipicolinic dihydrazide*, m. p. 280°; *dibenzylidinedipicolinic dihydrazide*, m. p. 297—298°; *divanillylidenedipicolinic dihydrazide*, m. p. 269—270°; *di*-o-*chlorobenzylidinedipicolinic dihydrazide*, m. p. 356—357°. Treatment with sodium nitrite and cold hydrochloric acid transformed dipicolinic dihydrazide into the comparatively stable *dipicolinic diazoimide*, m. p. 110—111°, which yielded the corresponding *diurethane*, m. p. 127°, when its alcoholiic solution was boiled. Mineral acids react very slowly with this compound; on the other hand, boiling alcoholic potash transforms it readily into 2 : 6-*diaminopyridine*, m. p. 180°.

The following derivatives of quinolinic acid were similarly prepared: *quinolinic dihydrazide*, m. p. 224°; *dibenzylidenequinolinic dihydrazide*, m. p. 160°; *di*-o-*chlorobenzylidenequinolinic dihydrazide*, m. p. 210—211°; *divanillylidinequinolinic hydrazide*, m. p. 252° (decomp.).

Methyl cinchomeronate under similar treatment yielded unexpectedly the *hydrazine* salt of hydrazidocinchomeronic acid, from which the free *acid*, $C_7H_7O_3N_3$, was readily isolated. Either of these substances, if heated at 365—370°, passes into the cyclic *hydrazide* of cinchomeronic acid (I), m. p. 365°. Blumenfeld (Abstr., 1896, i, 60) proposed the same formula for a substance which he obtained by the action of potassium hypobromite on cinchomeronic diamide. The two

(I.)  (II.) 

substances are not identical. The one isolated by Blumenfeld has probably the isomeric composition (II).

The action of phenylhydrazine on the esters of the pyridinecarboxylic acids was also studied. Ethyl picolinate and methyl dipicolinate, when boiled with phenylhydrazine, yielded *picolinic phenylhydrazide*, m. p. 184—185°, and *dipicolinic diphenylhydrazide*, m. p. 244°, respectively. Esters of nicotinic and *iso*nicotinic acids yielded only traces of phenylhydrazides. H. W.

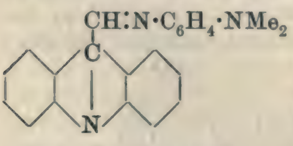
Preparation of Readily Soluble Double Compounds from Dialkylaminodimethylphenylpyrazolone, Caffeine, and Aromatic Acids. CHEMISCHE WERKE VORM. HEINRICH BYK (D.R.-P. 243069).—The following compounds which are readily soluble in water and of therapeutic value are obtained by heating together molecular proportions of the components in aqueous or alcoholic solution (or by fusing them together in the absence of solvents), and subsequently evaporating to dryness at a low temperature, or in a vacuum. (1) The *compound* from dimethylaminodimethylphenylpyrazolone (235 parts), caffeine (212 parts), and salicylic acid (138 parts); also a *compound* (2) when the salicylic acid is replaced by benzoic acid, and a *compound* (3) when replaced by phthalic acid. F. M. G. M.

Preparation of Derivatives of 4-Methylamino-1-phenyl-2:3-dimethyl-5-pyrazolone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 243197. Compare Abstr., 1910, i, 78, 340).—The therapeutically active *iso*valeryl derivatives of 4-methylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone can be prepared by the action of either *iso*valeryl chloride, or *iso*valeric acid, or anhydride, on the foregoing compound, or by the methylation of 4-*iso*valerylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone.

4-iso*Valerylmethylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* forms colourless crystals, m. p. 89—91°.

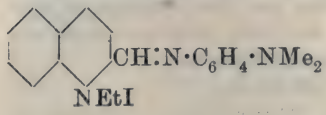
4-*Formylmethylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* has m. p. 107—108°, and can be employed for the preparation of formylaminoantipyrine, m. p. 189° (Abstr., 1897, i, 112). F. M. G. M.

Preparation of Condensation Products in the Pyridine, Quinoline, *iso*Quinoline, and Acridine Series. A. KAUFMANN (D.R.-P. 243078).—When cyclic ammonium bases containing a methyl group in the α- or γ-position to the ring nitrogen atom are heated with the *p*-nitroso-derivatives of tertiary aromatic amines in the presence of an alkaline condensing agent (such as piperidine, sodium, or potassium carbonate), they yield compounds which are readily hydrolysed to furnish an aldehyde and a primary amine.

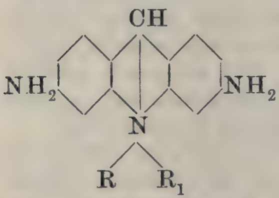


10-p-*Dimethylaminophenylazomethinacridine* (annexed formula), red crystals, m. p. 242—245°, was prepared by fusing *p*-nitrosodimethylaniline with 10-methylacridine at 100—120°; on hydrolysis it furnishes *p*-aminodimethylaniline and 10-acridylaldehyde.

2-p-*Dimethylaminophenylazomethinequinoline ethiodide* (annexed formula), green needles, m. p. 200° (approx. decomp.), was obtained in a similar manner from 2-methylquinoline ethiodide in alcoholic solution containing piperidine. F. M. G. M.



Preparation of 3:6-Diamino-10-alkylacridinium Compounds. LEOPOLD CASSELLA & Co. (D.R.-P. 243085).—It is found that 3:6-diaminoacridine (Abstr., 1911, i, 504) is readily acylated, and the ring nitrogen atom subsequently alkylated to yield (after hydrolysis) compounds of annexed general formula, where $R = CH_3$, C_2H_5, C_3H_7, or $C_6H_5CH_2$, and $R_1 = Cl$, SO_4H, or NO_3.



3:6-*Diamino-10-methylacridinium chloride*, red needles, was prepared in nitrobenzene solution by the action of methyl *p*-toluenesulphonate on the acylated base, followed by hydrolysis. This compound has a marked trypanocidal reaction, 1 c.c. of a solution of one gram in 5000—5500 c.c. water being effective in the case of an infected mouse.

F. M. G. M.

Derivatives of Azobenzene. OTTO N. WITT and EDUARD KOPETSCHNI (*Ber.*, 1912, **46**, 1134—1154).—The oxidation of *p*-nitroaniline in dilute sulphuric acid by ammonium persulphate at 40—45° yields a mixture of di-*p*-nitroazobenzene and di-*p*-nitroazoxybenzene, together with a little *p*-dinitrobenzene. (The last substance becomes the chief product, 75—77%, of the reaction when *p*-nitroaniline in concentrated sulphuric acid is slowly added to warm aqueous ammonium persulphate. *o*-Dinitrobenzene can be obtained from *o*-nitroaniline by a similar process.) The reduction of the preceding mixture by 44% sodium hydrosulphide in warm aqueous alcoholic solution yields di-*p*-aminoazobenzene ("diphenine"), the *diacetyl* derivative, m. p. 295—296°, pale yellow crystals, of which crystallises from acetic acid in yellow prisms containing $2CH_3{\cdot}CO_2H$, and does not experience the semidine transformation by treatment with alcoholic stannous chloride, but yields acetyl-*p*-phenylenediamine.

Di-*p*-nitrohydrazobenzene is formed as an intermediate product in the preceding preparation of di-*p*-aminoazobenzene. The paradoxical fact that the nitrated hydrazo-compound is converted into an aminoazo-compound in the presence of a mild reducing agent is the cause of the present investigation.

The authors confirm many of Green and Bearder's statements (Trans., 1911, **99**, 1960) regarding di-*p*-nitrohydrazobenzene. It is obtained best by reducing with aqueous ammonium hydrosulphide an acetone solution of dinitroazoxybenzene, or of the above-mentioned mixture of dinitroazoxybenzene and dinitroazobenzene. The substance is characterised by its extraordinarily labile nature, undergoing intra- and extra-molecular changes, whereby decomposition and condensation

products of very varied character are formed by the attack of different reagents. When heated in aqueous acetone on the water-bath with 50% potassium hydroxide and methyl sulphate, di-*p*-nitrohydrazobenzene yields p-*nitro*-p′-*methoxymethylaminoazobenzene*,

$$OMe\cdot NMe\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot NO_2,$$

m. p. 186·5°, garnet-red needles with a bluish-violet shimmer, p-*nitro*-p′-*methylaminoazobenzene*, $NO_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot NHMe$, m. p. 206—207° (*acetyl* derivative, m. p. 194—195°, orange-red needles), di-*p*-nitroazobenzene, and the *dimethyl ether* of di-*p*-nitrohydrazobenzene, $NO_2\cdot C_6H_4\cdot NMe\cdot NMe\cdot C_6H_4\cdot NO_2$, m. p. 177°, citron-yellow crystals. The last substance, which is the chief product of the reaction, is converted into *p*-nitromethylaniline by sodium hydrosulphide, and yields, by treatment with 60—70% sulphuric acid, an emerald-green solution which rapidly decomposes, formaldehyde, di-*p*-nitroazobenzene, and *p*-nitromethylaniline sulphate being formed.

When heated in alcoholic solution for seven hours at 170° in the absence of air, di-*p*-nitrohydrazobenzene yields di-*p*-nitroazobenzene, *p*-nitroaniline, *p*′-nitroaminoazobenzene, and bisnitrobenzeneazo-azobenzene, m. p. 294° (Green and Bearder give m. p. 285—286° [*loc. cit.*]). The last substance is converted by boiling aqueous alcoholic sodium hydrosulphide into *bisaminobenzeneazohydrazobenzene*,

$$N_2H_2(C_6H_4\cdot N_2\cdot C_6H_4\cdot NH_2)_2,$$

golden leaflets, which forms a sparingly soluble, violet *hydrochloride*, is converted into di-*p*-aminoazobenzene by boiling alcoholic ammonium hydrosulphide, and is oxidised in alcoholic solution by mercuric oxide to *bisaminobenzeneazo-azobenzene*,

$$NH_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NH_2,$$

garnet-red crystals, m. p. 294°, blackening at about 280°. This base, which is produced in quantity by the reaction of di-*p*-nitrohydrazobenzene and sodium sulphide in boiling 90% alcohol, forms a brown *hydrochloride* and an orange-red *acetyl* derivative, m. p. 361°, yields bisaminobenzeneazohydrazobenzene by reduction in sodium hydrosulphide, and can also be prepared by the reduction of *p*′-nitroaminoazobenzene by alcoholic sodium sulphide.

When warmed with concentrated sulphuric acid, di-*p*-nitrohydrazobenzene is converted, half into di-*p*-nitroazobenzene, and half into *p*-nitroaniline. When boiled, or heated at 105° under pressure, with alcohol and concentrated hydrochloric acid, di-*p*-nitrohydrazobenzene yields di-*p*-nitroazobenzene and an unstable, red *substance*, which is presumably p-*nitro*-p′-*hydroxylaminoazobenzene*,

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NH\cdot OH,$$

since it yields the above-mentioned *p*-nitro-*p*′-methoxymethylaminoazobenzene by methylation.

It will be seen from the preceding transformations that di-*p*-nitrohydrazobenzene exhibits the typical behaviour of a hydrazo-compound. Its peculiar behaviour is due to the mobility of the hydrogen atoms of the hydrazo-group. These hydrogen atoms are easily removed (whereby dinitroazobenzene is produced), and are then available either for the reduction of one or both nitro-groups to hydroxylamino- or amino-groups, or for fission of the azo-linking, whereby primary amines are produced. The conversion of dinitrohydrazobenzene into

diaminoazobenzene in the presence of mild reducing agents is hereby explained. C. S.

Heat Coagulation of Proteins. HARRIETTE CHICK and CHARLES J. MARTIN (*Brit. Assoc. Report*, 1911, 281—286).—Compare Abstr., 1911, i, 822. C. H. D.

The Refractive Indices of Solutions of Certain Proteins. VII. Salmine. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 11, 307—312).—The value of *a* (change in the refractive index of the solvent due to 1% of the protein) for salmine chloride and sulphate is identical within the experimental error, and $=0{\cdot}00172 \pm 0{\cdot}00009$.
W. D. H.

Direct Production of Carbamide from Proteins during Oxidation or Hydrolysis. ROBERT FOSSE (*Compt. rend.*, 1912, **154**, 1187—1188).—Béchamp (1856) stated that carbamide was formed during the oxidation of proteins by potassium permanganate, but his conclusions were controverted by Staedeler, Kolbe, and others. The following experiment, however, places the production of carbamide beyond doubt. Five grams of coagulated albumin are suspended in 100 c.c. of water, and treated gradually at 75—80° with 35 grams of potassium permanganate in portions of 5 grams. After filtration, the residue is washed with 150 c.c. of acetic acid, and the fitrate treated with 30 c.c. of a 5% solution of xanthhydrol, when dixanthylcarbamide separates in brilliant crystals (Abstr., 1908, i, 41). W. O. W.

Chemical Nature of Specific Oxygen Capacity in Hæmoglobin. RUDOLPH A. PETERS (*J. Physiol.*, 1912, **44**, 131—149).—Hæmoglobin, at any rate as regards its iron-containing portion, is identical throughout vertebrates, and it is to this part of the molecule that the oxygen is attached. The ratio oxygen to iron agrees within experimentol error with the value required for the reaction:

$$Fe + O_2 \rightleftarrows FeO_2.$$

W. D. H.

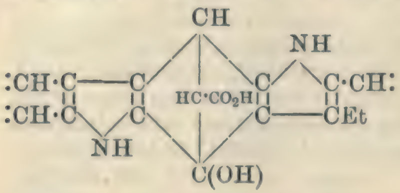
Constitution of the Coloured Constituent of the Pigment of Blood. II. OSCAR PILOTY and EDMUND DORMANN (*Annalen*, 1912, **388**, 313—329. Compare Abstr., 1911, i, 92).—Hitherto only basic substances have been isolated from the products of the reduction of hæmin by hydriodic acid and phosphonium iodide. Acidic products have now been isolated. The products of the reduction are basified and distilled with steam, and the residual liquor is filtered (the precipitate apparently contains hæmatopyrrolidinic acid) and extracted with ether after being acidified with dilute sulphuric acid. The ethereal extract contains phonopyrrolecarboxylic acid (the picrate of which has m. p. 157°, not 148°, as stated previously) and a new *acid*, $C_{10}H_{15}O_2N$, m. p. 105°, stout prisms (*picrate*, m. p. 142·5°), which is called *xanthopyrrolecarboxylic acid*, and receives the provisional formula:

$$CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}C{<}\begin{matrix}CEt-NH\\ \vert \\ CMe{:}CH\end{matrix},$$

a very small quantity of a third acid is also present, which has not yet

been isolated. An aqueous solution of xanthopyrrolecarboxylic acid at 50° reacts with nitrous acid to form an *isomeride*, m. p. 201—202° (decomp.), of the oxime of hæmatic acid.

In consequence of the discovery of xanthopyrrolecarboxylic acid, it is suggested that the right-hand half of the formula previously suggested for hæmatoporphyrin must be replaced by a complex such as the annexed; corresponding changes must be made in the suggested formulæ of mesoporphyrin and hæmin.



The presence of a complex such as, or similar to, this would account, not only for the production of butyric acid which appears to be formed during the decomposition of hæmatoporphyrin and hæmin, but also for the presence of phyllopyrrole (2 : 3 : 5-trimethyl-4-ethylpyrrole) in the hæmopyrrole mixture (Willstätter and Asahina, this vol., i, 41).

The mean molecular weight of hæmatoporphyrin, determined in pyridine by the ebullioscopic method, is 1150; the value required by the formula suggested in this paper is 1168. C. S.

Echinochrome, a Red Substance in Sea Urchins. J. F. McClendon (*J. Biol. Chem.*, 1912, 11, 435—441).—Just as hæmolytic agents cause hæmoglobin to leave red corpuscles, so do cytolytic agents cause echinochrome to leave the cells which contain the chromatophores which are coloured red by echinochrome. The pigment before extraction shows no absorption bands, but after extraction with ether, alcohol, or water two spectroscopic bands are seen, the positions of which vary with the solvent, but the measurements given are approximately the same as previously stated by McMunn. On the addition of iodine in potassium iodide, it is obtained in crystalline form, as A. P. Mathews found. The percentages of carbon, hydrogen, and nitrogen vary with the methods used. It is precipitated by alkalis in alcohol, also by phosphomolybdic and phosphotungstic acids, but not by tannin. It is probably amphoteric. No evidence that it acts as an oxygen carrier was found. Echinochrome is probably held in the same way as chlorophyll is held in the plant cell. W. D. H.

Keratin of Elephant Epidermis. Hans Buchtala (*Zeitsch. physiol. Chem.*, 1912, 78, 55—61).—The purified air dry material contained 2·66% of ash comprising considerable quantities of iron. The total nitrogen was 14·26%, distributed as ammonia, 1·47%, melanin, 0·2%, monoamino-acids, 12·25%, diamino-acids, 0·32%.

On hydrolysis with hydrochloric acid the following results were obtained: glycine, 8·33%; alanine, 5·07%; valine, 2·43%; leucine, 3·6%; glutamic acid, 10·2%; phenylalanine, 2·33%; tyrosine, 5·2%; cystine, 4·70%.

About 10% of a residue remained on hydrolysis somewhat resembling asphalt, part of which consisted of fatty acids. E. F. A.

Action of Light and Hydrogen Peroxide on Proteins and Amino-acids. JEAN EFFRONT (*Compt. rend.*, 1912, **154**, 1111—1114).—When sterile solutions of peptone are exposed to sunlight, decomposition occurs, and hydrogen peroxide, nitrates, ammonia, and volatile acids appear in the liquid. The destruction of the peptone appears to be due to the hydrogen peroxide, since this substance brings about rapid and complete destruction of peptones and amino-acids, the transformation being analogous to that effected by proteolytic bacteria and amidases. W. O. W.

Lipoids. XV. The Drying of Tissues and Blood for the Preparation of Lipoids. SIGMUND FRÄNKEL and ALADAR ELFER (*Biochem. Zeitsch.*, 1912, **40**, 138—144).—The authors have found that anhydrous sodium phosphate is preferable both to sodium and calcium sulphates for the drying of tissues. Less salt is used, and there is the further advantage that the hydrated salt is still liquid at 37°. The salt is, therefore, ground up with the tissue in warmed vessels, and then pressed in warm cloths. The material can be thus obtained in a dried form, which can be readily powdered without a great increase in bulk. S. B. S.

Notes. [Tryptophan. Selective Absorption. Nomenclature.] EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, **78**, 159—163).—I. *Formation of a Brown Pigment from Tryptophan.*—Tryptophan mother liquors darken when kept for a long time, and finally a small quantity of a brown substance separates. This is soluble in both alkali and acid; it contains 38·3% C, 4·83% H, and 11·54% N. When burnt an odour of indole is perceptible. It is considered to be a condensation product derived from tryptophan or from a derivative of this. It no longer gives a coloration with glyoxylic acid and concentrated sulphuric acid.

II. The fluid obtained from the *spongiosa* of the head of the femur gave a precipitate of protein which contained a considerable proportion of tryptophan—above 3%. Tryptophan was also obtained from a compound present in the urine in a case of melanuria.

III. The behaviour of pieces of spinal nerve, sympathetic ganglion tissue, and of striped and smooth muscle fibre towards *l*-, *d*-, and *dl*-adrenaline has been studied with the object of detecting selective absorption by the tissue. No such absorption could be detected.

IV. *Nomenclature Simplification.*—Halliburton's suggestion to use the terms caseinogen and casein is supported.

It is proposed to use hæmatin instead of hæmochromogen. The general name sterol is proposed for all compounds of the cholesterol group. E. F. A.

The Influence of Colloids on Ferments. II. The Action of Inorganic Colloids on Trypsin. LUDWIG PINCUSSOHN (*Biochem. Zeitsch.*, 1912, **40**, 308—313).—Metallic colloids containing albumin as protective colloid, as well as oxides and peroxides, exert an inhibitory action on trypsin, and when in sufficiently high concentration, completely stop the ferment action. Metallic colloids prepared by the electrical dispersion method stimulate, on the other hand, tryptic

action, the concentration in which this action takes place being characteristic for each individual metal. S. B. S.

The Action of Trypsin. I. Hydrolysis of Caseinogen by Trypsin. E. H. WALTERS (*J. Biol. Chem.*, 1912, 11, 267—306).—The method of estimating the velocity with which caseinogen is hydrolysed by determining the nitrogen in the undigested portion after precipitation with acetic acid yields accurate results. Precipitation by acetic acid is hastened, and a clear filtrate assured by adding first a slight excess of alkali. The relation between the time of hydrolysis and the amount of "basic" sodium caseinogenate hydrolysed is what would be expected from the unimolecular formula. The velocity with which basic sodium caseinogenate is hydrolysed by trypsin is directly proportional to the concentration of the enzyme. The velocity constant decreases slightly as the concentration of the substrate increases. The nature of the base combined with caseinogen has no influence. There is no relation between the degree of dissociation and the rate with which basic caseinogenates are hydrolysed by trypsin. Rapid auto-hydrolysis occurs in solutions of neutral and basic caseinogenates of the alkalis and alkaline earths. W. D. H.

Comparative Hydrolysis of Sucrose by Various Acids in Presence of the Invertase of Aspergillus Niger. GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Bull. Soc. chim.*, 1912, [iv], 11, 464—468. Compare this vol., i, 327).—The results obtained resemble generally those already recorded for yeast invertase (*loc. cit.*) Aspergillus invertase is, however, more susceptible to the influence of acid radicles than yeast invertase, and consequently the disturbing influences shown in the previous work are more accentuated in this. The optimum concentrations for most acids are higher for Aspergillus invertase than for yeast invertase, but they are identical for propionic acid, and less for nitric, formic, and phosphoric acids. These differences are not due to the salts present in the enzyme preparations used, and seem to be traceable to the influence of the acid on the enzyme itself. T. A. H.

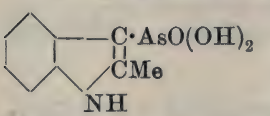
Action of Emulsin on Salicin in Alcoholic Solution. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 154, 944—946; *J. Pharm. Chim.*, 1912, [vii], 5, 388—392. Compare Abstr., 1911, i, 1053).—An examination of another case in which, contrary to the usual view, alcohol does not inhibit the hydrolytic activity of an enzyme. Unlike gentiopicrin, salicin is not hydrolysed by emulsin in presence of 95° alcohol at the ordinary temperature. With alcohol of 90° strength, hydrolysis occurs, and equilibrium is attained after forty-eight days, when 37% of the glucoside has been decomposed. As the strength of the alcohol is diminished, equilibrium is more rapidly attained, and a greater proportion of the salicin undergoes hydrolysis. W. O. W.

Studies on Enzyme Action. I. Some Experiments with the Castor Bean Lipase. K. GEORGE FALK and JOHN M. NELSON (*J. Amer. Chem. Soc.*, 1912, 34, 735—745).—A comparative study has

been made of the hydrolysis of methyl acetate, ethyl butyrate, and olive oil by the lipase of castor seed. The addition of small quantities of alkali hydroxide at the beginning of the action does not affect the subsequent hydrolysis in the case of methyl acetate, but diminishes the rate of action in that of ethyl butyrate. The results obtained with olive oil do not lead to any definite conclusion. In ether, saturated with water, or acetone, containing a small quantity of water, methyl acetate is hydrolysed by lipase to a considerable extent both at the ordinary temperature and at the b. p. of the liquid. It has been found that small quantities of an active constituent can be extracted from the lipase by water and by ethyl acetate. By the electrolysis of an aqueous suspension of the lipase preparation, a substance was produced in the anode solution, probably by oxidation, which showed marked hydrolytic activity. E. G.

Preparation of Arsinic Acids of the Indole Series. C. F. BOEHRINGER & SÖHNE (D.R.-P. 240793).—When indoles are heated with arsenic acid in either aqueous or organic solvents, substitution occurs in the para-position to the nitrogen atom in the indole ring; this new type of therapeutically active compounds crystallise readily, and form well characterised salts with either organic or inorganic bases.

2-*Methylindole*-3-*arsinic acid* (annexed formula), colourless needles,



m. p. 180—182°, was obtained in 93% yield by gently warming anhydrous arsenic acid (28·4 parts) with 6 parts of water, and adding 2-methylindole (13·1 parts) with continual stirring, when the whole solidifies to a crystalline mass. The *sodium* salt, $C_9H_9O_3NAsNa,2\frac{1}{2}H_2O$, has m. p. 225—235° (decomp.); the *quinine* salt,

$$C_{20}H_{24}O_2N_2,C_9H_{10}O_3NAs,2\tfrac{1}{2}H_2O,$$

sinters at 155°, m. p. 170—172°.

a-Naphthindolearsinic acid, $C_{12}H_{12}O_3NAs$, prepared in boiling absolute alcohol and toluene solution, is obtained in 56% yield.

5-*Chloro*-2-*methylindole*-3-*arsinic acid*, $C_9H_9O_3NClAs$, m. p. 185—186° (decomp.), is similarly prepared from 5-chloro-2-methylindole.

F. M. G. M.

3:3′-Diamino-4:4′-dihydroxyarsenobenzene Hydrochloride (Salvarsan) and Allied Substances. PAUL EHRLICH and ALFRED BERTHEIM (*Ber.*, 1912, 45, 756—766).—3-Nitro-4-hydroxyphenylarsinic acid is reduced by methyl alcohol and 4% sodium amalgam to 3-*amino*-4-*hydroxyphenylarsinic acid*, $NH_2·C_6H_3(OH)·AsO_3H_2$, which crystallises in small prisms, is sparingly soluble, darkens above 170°, and decomposes without melting, possesses reducing properties, and forms a *sodium* salt, $C_6H_7O_4NAsNa,H_2O$ (or $2H_2O$). By treating its solution in dilute hydrochloric acid and potassium iodide with sulphur dioxide, it is converted into (impure) 3-*amino*-4-*hydroxyphenylarsenic oxide*, $NH_2·C_6H_3(OH)·AsO$, which is soluble in acids and in alkali

hydroxides or carbonates, and forms an extremely soluble *hydrochloride*, $C_6H_6O_2NAs,HCl,\frac{1}{2}EtOH$.

3 : 3′-*Diamino*-4 : 4′-*dihydroxyarsenobenzene hydrochloride*,

$$As_2[C_6H_3(OH)\cdot NH_2,HCl]_2,$$

can be prepared by reducing the preceding compound with stannous chloride and hydrochloric acid, or by treating 3-nitro-4-hydroxyphenylarsinic acid in an aqueous solution of magnesium chloride with alkaline sodium hyposulphite at 55—60°, and acting on the isolated product with methyl-alcoholic hydrogen chloride. As thus prepared, the hydrochloride contains MeOH, and decomposes at 185—195°. It is easily soluble in water, but not in concentrated hydrochloric acid, and by treatment with sodium hydroxide yields 3 : 3′-*diamino*-4 : 4′-*dihydroxyarsenobenzene*, which is soluble in an excess of the alkali.

A delicate test for the hydrochloride is to treat it with *p*-dimethylaminobenzaldehyde in dilute hydrochloric acid, containing some mercuric chloride, whereby an orange coloration, and subsequently an orange precipitate, are produced

Salvarsan is very readily oxidised in the air, yielding the aminohydroxyphenylarsenic oxide. This fact is important from the physiological side, because the oxide is about twenty times as poisonous as salvarsan. By more energetic oxidation, for example, by hydrogen peroxide or iodine solution, salvarsan is converted into aminohydroxyphenylarsinic acid.

Solutions of salvarsan in water, methyl alcohol, or aqueous alkalis are very unstable. Even with the complete exclusion of oxygen, they become red and finally colourless, a complex, reddish-brown precipitate being formed. C. S.

Isomorphism in Organo-metallic Compounds. I. Derivatives of Quadrivalent Metals. PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 321—325).—Determinations of the fusion curves of binary mixtures of the tetraphenyl derivatives of silicon, tin, and lead show that these three compounds are isomorphous, and thus afford further evidence of the close relationship of lead to silicon and tin.

Tetraphenylsilicon, m. p. 233°, when mixed with varying quantities of tin tetraphenyl, begins to solidify at a slightly higher temperature than that at which solidification is complete, until the quantity of the silicon compound falls to 33%, when the mixture solidifies at a constant temperature of 221°. The corresponding figures for a mixture of tetraphenylsilicon and lead tetraphenyl are 34% and 218·8°. A mixture of tin tetraphenyl, m. p. 225·7°, and lead tetraphenyl, m. p. 227·7°, on the contrary, shows no eutectic point, and the crystals which separate are always richer in lead than the liquid. From these results the conclusion is drawn that these three compounds are similarly constituted and of very similar crystallographic form, and that they are able to form mixed crystals in all proportions. T. A. H.

Organic Chemistry.

The Formation of the Chief Constituents of Petroleum. CARL ENGLER (*Petroleum*, 1912, 7, 399—403).—The author discusses the probable and possible origin of petroleum by means of polymerisation and depolymerisation of the decayed complex organic constituents of plant and animal remains.

The following distinct "phases" of bitumen are discussed: anabitumen, polybitumen, catabitumen, ecgonobitumen, and oxybitumen, and from these are traced the possible formation of the different constituents contained in petroleum. F. M. G. M.

Preparation of Butadiene and its Homologues. GEZA AUSTERWEIL (D.R.-P. 245180).—Isoprene, accompanied by varying quantities of butadiene and mono- and di-methylbutadienes, is obtained when vinyl bromide (107 parts) is slowly dropped into a mixture of magnesium (24 parts) and ether (400 c.c.), followed by the addition of β-chloropropylene (75 parts). After heating during a short period, the mixture is shaken with ice and dilute acetic acid, and the components are subsequently separated by distillation. The reaction takes place according to the equation:

$$2CH_2{:}CRR' + Mg = MgR_2 + CH_2{:}CR'{\cdot}CR'{:}CH_2,$$

where R is a halogen atom, and R′, alkyl, aryl, or hydrogen.

F. M. G. M.

Pyrogenic Acetylene Condensations. RICHARD MEYER (*Ber.*, 1912, 45, 1609—1633).—The formation of benzene hydrocarbons by the dry distillation of coal is probably largely due to the aromatic nature of coal itself (compare Burgess and Wheeler, Trans., 1911, 99, 649, and Pictet and Ramseyer, Abstr., 1911, i, 850), but the condensation of acetylene undoubtedly plays an important part. Berthelot expressed the opinion that coal-gas acetylene owes its origin to the decomposition of methane, but it has been shown that a much higher temperature is necessary for this change than for the production of tar, whilst the present author believes that the reverse action (conversion of acetylene into methane) takes place to a great extent. This, in conjunction with the ready condensation to aromatic hydrocarbons, would explain why acetylene occurs in only small quantities in coal gas.

The experiments of Berthelot have now been repeated on a large scale under carefully controlled conditions, and the resulting tar has been subjected to exact investigation. The apparatus consists in the main of two vertical tube furnaces heated electrically, each provided with an electric resistance thermometer and a number of receivers for the tar. The temperature of the first is maintained at 640—650°, and that of the second at 800°, very careful regulation being made possible by a number of electrical appliances. The acetylene is diluted with the same volume of hydrogen, since it otherwise inflames and deposits charcoal, but, nevertheless, a considerable proportion is decomposed

into methane. After passing through the furnaces, the gases are used to dilute further volumes of acetylene. The whole apparatus is placed in circuit with an exhaust, which, when once regulated, is made to work automatically, so that the gases circulate at a constant speed of about 40 litres per hour, a particle of acetylene spending about one minute in each furnace. In one experiment 1732 litres of mixed gases, containing 866 litres, or 952 grams, of acetylene, gave 601 grams of tar, that is, 63%. The loss is due to the formation of methane and hydrogen, and the excess of these gases must be removed from time to time.

The tar from the first furnace is richer in light oils, and that from the second in high-molecular hydrocarbons. They have been submitted to repeated fractionation and crystallisation, and any unsaturated hydrocarbons have been removed by bromine water. Benzene forms about one-fifth of the product. Electric heating was resorted to in order to thoroughly fractionate the portion boiling from 90° to 150°, and toluene, which Berthelot did not find, was definitely identified, whilst xylenes could not be characterised. The next higher fraction, up to 200°, was found to absorb bromine, the product on steam distillation giving bromohydroxyindene, m. p. 129°, from which indene was obtained by the method of Weissgerber and Dombrowsky (Abstr., 1909, i, 219). Except in boiling point (179°) this has many of the properties of styrene, which could not be detected, and Berthelot was probably mistaken in assuming the formation of the latter.

The residue from the separation of indene, and the highest fractions, were redistilled, and the portion boiling between 200° and 300° was separated by steam distillation into naphthalene, diphenyl, and fluorene. Similarly, from the fraction 300—450° a small amount of anthracene together with pyrene and chrysene were obtained. These nine hydrocarbons have been most precisely characterised, and have all been found in coal-tar.

J. C. W.

Hypoiodites in the Formation of Iodoform. A. PIERONI (*Gazzetta*, 1912, **42**, i, 534—536).—It is generally assumed that the formation of iodoform from acetone or compounds containing the group $CH_3·CO·C$ or $CH_3·CH(OH)·C$ is brought about by the action of hypoiodites, just as chloroform is given by hypochlorites. If the iodoform produced by the interaction of an energetic base (for example, sodium hydroxide), iodine, and acetone really depends on the quantity of hypoiodite present, the amounts of iodoform which can be obtained must be proportional to the quantities of hypoiodite obtainable from the base and the iodine. Schwicker (Abstr., 1895, ii, 213) showed that the reaction according to which hypoiodites are transformed in alkaline solution is of the third order; this author determined the quantity of hypoiodite formed in the reaction between a base and a solution of iodine in potassium iodide by titrimetric estimation of the iodine liberated by potassium hydrogen carbonate. The present author estimates the hypoiodite with acetone in alkaline solution, his results showing that the transformation of the hypoiodite is a reaction of the second order, and hence that the formation of iodoform is due to the action of the hypoiodite on the acetone.

The values of K for the formation of iodoform are of the same order of magnitude as those obtained by Schwicker. T. H. P.

Condensation of the Sodium Derivatives of Primary Alcohols with Secondary Alcohols. MARCEL GUERBET (*Compt. rend.*, 1912, **154**, 1357—1359. Compare Abstr., 1910, i, 149, 454).—When secondary alcohols are heated with the sodium derivatives of primary alcohols, sodium hydroxide is formed together with a secondary alcohol in which the alkyl group of the primary alcohol is joined to the carbon atom next to that to which the hydroxyl group is attached.

*iso*Propyl alcohol when heated with sodium *iso*amyloxide at 220—230° forms *β-methylheptane-ζ-ol*, b. p. 172—173°, D^0 0·8329, which under the action of potassium hydroxide at 230° yields hydrogen and an *alcohol*, $C_{16}H_{34}O$, b. p. 160—165°/15 mm., together with small quantities of formic acid and of an acid, the *barium* salt of which has the formula $(C_7H_{13}O_2)_2Ba$. It thus appears to be a secondary alcohol. This view is supported by its velocity of esterification, 18·8. When oxidised, it yields β-methylheptane-ζ-one, b. p. 170—171°, which gives a crystalline *compound* with sodium hydrogen sulphite, and was further identified by oxidising it to acetic acid and δ-methylvaleric acid. Similarly, *γ-propyloctane-β-ol* results from the interaction of propyl and octylic alcohols in the presence of sodium. It has b. p. 234—235°, m. p. +5°, D^{17} 0·831, velocity of esterification, 16·4. Its *acetic* ester has b. p. 246—248°. When heated at 230° with an excess of potassium hydroxide, it yields hydrogen, an *alcohol*, b. p. above 300° (decomp.), and small quantities of formic and octoic acids. On oxidation, it yields *γ-propyloctane-β-one*, b. p. 230—231°, D^0 0·8405, which combines with sodium hydrogen sulphite, and can be further oxidised to acetic acid and propyl amyl ketone, b. p. 187—188°.

H. W.

A Mode of Formation of Acraldehyde. WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1912, **154**, 1353—1354).—Acraldehyde is formed during the dry distillation of sodium formate. It was identified by transforming it into acraldehyde-ammonia, which yielded picoline when subjected to dry distillation. The platinichloride of the latter was analysed. H. W.

Condensation of Butyrone with Organo-magnesium Compounds. MARCEL MURAT and GAËTAN AMOUROUX (*J. Pharm. Chim.*, 1912, [viii], 5, 473—478).—A number of tertiary alcohols obtained by treating dipropyl ketone with the Grignard reagent are described.

*Dipropyl*iso*amylcarbinol*, $C_5H_{11}\cdot CPr_2{}^{\alpha}\cdot OH$, D^0 0·8548, D^{19} 0·8388, n_D 1·443, b. p. 114—116°/17 mm., obtained by condensing dipropyl ketone with magnesium *iso*amyl bromide, is a viscous, pleasant-smelling liquid. On catalytic dehydration with alumina, it yields a *hydrocarbon*, $C_5H_{10}{:}CPr_2{}^{\alpha}$ or $C_5H_{11}\cdot CPr^{\alpha}{:}C_3H_6$, D^0 0·7851, D^{21} 0·7672, n_D 1·434, b. p. 191—192°/760 mm., as a colourless, mobile liquid with a faintly alliaceous odour. On catalytic reduction over hot nickel this

olefinic hydrocarbon yields *dipropylisoamylmethane* [δ-iso*amylheptane*], D^{14} 0·7538, n_D 1·425, b. p. 189—190°/760 mm.

Dipropylisobutylcarbinol, D^0 0·8577, D^{14} 0·8445, n_D 1·439, b. p. 110—114°/20 mm., is a colourless, syrupy liquid. It is decomposed by hot alumina, giving a *hydrocarbon*, $C_{11}H_{22}$, D^{15} 0·7710, n_D 1·433, b. p. 180—183°/760 mm., which is colourless and of disagreeable odour.

Phenyldipropylcarbinol, D^0 0·9589, D^{15} 0·9470, n_D 1·516, b. p. 134°/26 mm. is a colourless, viscid liquid; the *acetyl* derivative has D^{15} 0·8973 and b. p. 160°/19 mm. (decomp.). On dehydration, δ-*phenyl*-Δ^γ-*heptene*, $CPr^a{\cdot}Ph{:}C_3H_6$, D^{15} 0·8855, n^{15} 1·522, b. p. 228°/760 mm., is formed as a colourless liquid, which with nitrosyl chloride at −10° gives a colourless *nitrosochloride*, m. p. 112° (decomp.).

Benzyldipropylcarbinol, D^0 0·9506, D^{19} 0·9386, n_D 1·513, b. p. 161—164°/30 mm., is a viscous liquid with a pleasant odour. On dehydration by hot alumina, it yields a *hydrocarbon*, D^{19} 0·902, n_D 1·523, b. p. 246—248°/760 mm., which on catalytic reduction over nickel yields δ-*benzylheptane*, $CH_2Ph{\cdot}CHPr_2^a$, D^{14} 0·854, n_D 1·487, b. p. 241—244°/756 mm., and with nitrosyl chloride furnishes a *nitrosochloride*, m. p. 115°.

cyclo*Hexyldipropylcarbinol*, D^0 0·9157, D^{19} 0·9025, n_D 1·469, b. p. 128—130°/11 mm., 256—260°/760 mm., is a colourless, syrupy liquid with a fruity odour, and gives an *acetyl* ester, b. p. 133—136°/5 mm. On dehydration, the alcohol furnishes an ethylenic *hydrocarbon*, D^{21} 0·8441, n_D 1·467, b. p. 226—228°/760 mm., which gives a *nitrosochloride*, m. p. 110° (decomp.). On reduction, this hydrocarbon furnishes δ-cyclo*hexylheptane*, D^{13} 0·8468, n_D 1·467, b. p. 228°/760 mm., a colourless, almost inodorous liquid. T. A. H.

Metallic Glycoloxides. E. CHABLAY (*Compt. rend.*, 1912, **154**, 1507—1509).—Ethylene glycol dissolved in liquid ammonia reacts with a solution of sodium, potassium, or lithium in the same medium at −50°, giving a monometallic glycoloxide, $OM{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. The sodium and potassium derivatives are crystalline, whilst the *lithium* salt is a white, amorphous powder. These substances when heated in a current of hydrogen begin to lose glycol at 165°, and at 200° are rapidly converted into the corresponding dimetallic compounds, $OM{\cdot}CH_2{\cdot}CH_2{\cdot}OM$.

If, in the above reaction, a bivalent metal is substituted for the alkali metal, theoretically two types of derivatives should be possible.

$$\text{(I.)}\ \begin{array}{ccc} CH_2{\cdot}O{-}M''{-}O{\cdot}CH_2 \\ | \qquad\qquad\qquad | \\ CH_2{-}OH \qquad CH_2{\cdot}OH \end{array} \qquad \text{(II.)}\ \begin{array}{l} CH_2O \\ | \\ CH_2O \end{array}\!\!>M''.$$

Only the derivatives of type (II) can be obtained, and these have been prepared in the case of *calcium*, *strontium*, *barium*, and *lead*.

Monosodium ethyleneglycoloxide and thallium nitrate interact immediately in the cold, forming *dithallium ethyleneglycoloxide*,

$$OTl{\cdot}CH_2{\cdot}CH_2{\cdot}OTl.$$

W. G.

Decomposition of Glycerol by Ultra-violet Rays. VICTOR HENRI and ALBERT RANC (*Compt. rend.*, 1912, **154**, 1261—1263. Compare Abstr., 1910, i, 652; 1911, i, 255; ii, 833).—It is now

shown that when a solution of glycerol in water at a temperature of 80° is exposed to ultra-violet rays from a lamp of much higher intensity than that formerly used, formaldehyde is formed, together with other aldehydic substances giving the reactions of Legal and Lewin, and the liquid becomes acid. The action is accelerated by hydrogen peroxide. T. A. H.

β-Aminoethyl Mercaptan. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1912, **45**, 1643—1654).—The free base has been liberated from the hydrochloride (Abstr., 1891, 815), some derivatives have been studied, and in attempting to find a more convenient method for the production of the parent substance, ethyl mercaptophthalimide (Abstr., 1889, 870), a basic isomeride of this substance has been discovered.

β-Aminoethyl mercaptan, $HS\cdot CH_2\cdot CH_2\cdot NH_2$, sublimes in a vacuum in colourless, rhombic crystals, m. p. 99—100°; it is strongly alkaline in water, undergoes oxidation in the air to diaminodiethyl disulphide, and forms a *picrate*, m. p. 125—126°. The hydrochloride condenses with ethylene chlorohydrin in presence of sodium methoxide, yielding an oily hydroxy base, $NH_2\cdot C_2H_4\cdot S\cdot C_2H_4\cdot OH$, which saturated hydrochloric acid, in a sealed tube, converts into the *hydrochloride* of *chloroaminodiethyl sulphide*, $Cl\cdot C_2H_4\cdot S\cdot C_2H_4\cdot NH_2,HCl$, which crystallises from acetone, m. p. 77—78°, and forms a readily soluble *picrate*, m. p. 105°. The chloro-base could not be condensed to form the ring compound thiomorpholine.

Instead of treating bromoethylphthalimide with potassium hydrosulphide, which complicates the preparation of ethyl mercaptophthalimide through the formation of diphthalylamidoethyl sulphide (*loc. cit.*), it has been heated with potassium ethyl xanthate. The *phthalimidoethyl xanthate*, $C_8H_4O_2{:}N\cdot C_2H_4\cdot S\cdot CS\cdot OEt$, was readily obtained in tufted needles, m. p. 80°, but could only be hydrolysed by boiling hydrobromic acid, yielding then a small amount of ethyl mercaptophthalimide, but chiefly the *hydrobromide* of an isomeric base, $C_{10}H_9O_2NS,HBr$, m. p. 218°. The base itself, which proved to be the *anhydride* of *N-β-ethyl mercaptophthalamic acid*, $C_6H_4<\begin{matrix}CO\cdot NH\cdot CH_2\\ CO{-}S{-}CH_2\end{matrix}$, is easily liberated by dilute alkali in short prisms, m. p. 147°, which dissolve in stronger alkali, the *potassium* salt, $C_{10}H_8NSO_2K$, forming shining flakes. The *hydrochloride*, m. p. 207°, the *platinichloride*, and the *picrate*, m. p. 181°, are described, and by the action of sodium nitrite the *nitrosoamine*, $C_6H_4<\begin{matrix}CO\cdot N(NO)\cdot CH_2\\ CO{-\!-}S{-\!-}CH_2\end{matrix}$, has been obtained in needles, m. p. 157—158°, which revert to the imine when boiled with alcohol or hydrochloric acid, but decompose when warmed with dilute alkalis into phthalic acid, nitrogen, acetylene, hydrogen sulphide, and a trace of what is probably ethylene sulphide.

In certain respects this thio-base differs from its analogue, the anhydride of hydroxyethylphthalamic acid (Abstr., 1905, i, 650); it decomposes when heated; it is not hydrolysed by boiling water, but passed into the isomeric ethyl mercaptophthalimide; and when heated with hydrochloric acid it is not chlorinated, but is converted into the

isomeride with partial hydrolysis into phthalic acid and aminoethylmercaptan.

Conversely, when ethyl mercaptophthalimide is heated with dilute alkali it is converted into *ethylmercaptophthalamic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot SH,$$

crystallising from ethyl acetate in leaflets which melt and change into the imide at 114—115°, but which are converted into the anhydride when heated with fuming hydrobromic acid. This agent has the same effect on thiocarbimidoethylphthalimide (Abstr., 1891, 1216) and on *phthaliminoethyl a-thiocarbamate*, $C_8H_4O_2\colon N\cdot C_2H_4\cdot S\cdot CO\cdot NH_2$, which substance is obtained in colourless needles, m. p. 149°, from the thiocarbamido-compound by the action of sulphuric acid.

Methyl iodide converts the base, $C_{10}H_9NSO_2$, into the *hydriodide* of *ethylmercaptophthalmethylamic anhydride*, $C_{11}H_{11}O_2NS,HI$, m. p. 221—222°, the *monohydrate* crystallising from hot water in long needles, and the *picrate* melting at 188°. The free base could not be obtained, alkali producing *ethylmercaptophthalmethylamic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot NMe\cdot C_2H_4\cdot SH$, in thin tablets, m. p. 167—168°; it is reconverted into the base by acetyl chloride, and on prolonged boiling with water, it changes into a syrup which probably contains methylaminoethyl mercaptan phthalate, $C_8H_6O_4,NHMe\cdot C_2H_4\cdot SH$, since hydrochloric acid precipitates phthalic acid from its solution. The *β-methylaminoethyl mercaptan*, $NHMe\cdot C_2H_4\cdot SH$, is more readily obtained by the hydrolysis of the hydriodide of the methyl base by means of hydrochloric acid in a sealed tube. It forms a very hygroscopic, crystalline mass, giving a *picrate*, m. p. 90—91°, the mother liquor from which, after many days, deposits the *picrate*, m. p. 157°, of *di-β-methylaminoethyl disulphide*, $S_2(C_2H_4\cdot NHMe)_2$, a base which is quickly obtained as a colourless oil by the oxidation of the mercaptan with iodine, and forms a *hydrochloride*, $C_6H_{16}N_2S_2,2HCl$, m. p. 204—205°. J. C. W.

Green and Violet Complex Chromic Acetates. RUDOLF F. WEINLAND and ERNST BÜTTNER (*Zeitsch. anorg. Chem.*, 1912, 75, 293—370. Compare Abstr., 1910, i, 503; Weinland and Dinkelacker, Abstr., 1909, i, 757; Werner, Abstr., 1908, i, 935).—Salts of the green hexa-acetatotriamminetrichromic base are prepared by passing dry ammonia into a solution of a salt of the hexa-acetato-base in absolute alcohol. The reaction is complete in a day, and one of the sparingly soluble salts may then be precipitated. The *iodide*, $\left[\begin{matrix}(OAc)_6\\ Cr_3(OH)_2\\ (NH_3)_3\end{matrix}\right]I$, is best suited to the qualitative detection, and forms hexagonal tablets. None of the salts contain less than six acetic residues. The bromide contains H_2O, and the chloride $2H_2O$. Salts with colourless acids are pale green in the solid state, and olive-green in solution. As with pyridine, the strength of the base is increased by the introduction of the ammonia, and the list of salts prepared includes a cyanide and a carbonate.

Werner's hexa-acetatomonoamminetrichromic salts may be more readily prepared by heating hexa-acetatotrichromic diacetate with

ammonium acetate on a water-bath. The salts of the monoammine base are then separated by precipitation as iodide or as perchlorate, and then have the formulæ: $\left[\begin{matrix}(OAc)_6\\ Cr_3(OH)_2\\ NH_3\end{matrix}\right]I,2H_2O$ (or $ClO_4,3H_2O$), whilst the thiocyanate and mercurichloride contain more ammonia.

When the attempt is made to prepare hexa-acetatotrichromic thiocyanate, a green, sparingly soluble salt is obtained, in which a thiocyano-group has entered the complex. It dissolves in alcohol and also in dilute alkalis, and may possibly be an acid, $\left[\begin{matrix}(OAc)_6\\ Cr_3(OH)_3\\ CNS\end{matrix}\right]H,2H_2O$. It dissolves in pyridine, yielding hexa-acetatotripyridine-trichromic thiocyanate.

Salts of a violet penta-acetatotrichromic base are obtained by repeated evaporation of the green salts on the water-bath. The principal salt of the series is the *monoacetate*, $\left[\begin{matrix}(OAc)_5\\ Cr_3(OH)_3\\ H_2O\end{matrix}\right]OAc,11H_2O$, which forms dark violet rhombohedra. It may be obtained directly from the green acetate, or by hydrolysis of any of the higher acetates of this series. At 17·5° it dissolves in 21·5 parts of water. Methyl alcohol removes $6H_2O$, leaving a crystalline residue of the same salt with $5H_2O$. The constitution is shown to be that given above, by means of the chemical reactions, molecular weight, and electrical conductivity. A double salt of the mono- and di-acetate, with $10H_2O$, is most easily prepared, and forms dark violet needles. The triacetate crystallises in prisms, $\left[\begin{matrix}(OAc)_5\\ Cr_3(OH)_2\\ H_2O\end{matrix}\right]\begin{matrix}(OAc)_2\\ HOAc\end{matrix},H_2O$, and also with 3 more mols. H_2O. The tetra-acetate forms thin tablets. The chloride-acetate, bromide-acetate, and sulphate-acetate have also been prepared, several different double salts being found to exist. The formate-acetate, from the mono-acetate and 85% formic acid, contains $8H_2O$ outside the complex, and forms violet, readily soluble needles. A double salt of the mono-acetate of the violet penta-aceto-base and the mono-acetate of the green hexa-aceto-base crystallises in greyish-violet prisms.

Gussmann's triacetatotrichromic acetate (Abstr., 1911, i, 103) is more conveniently prepared by repeated evaporation of the green hexa-acetatodiacetate with water, and then forms long, tetragonal bipyramids, $\left[Cr_3\begin{matrix}(OAc)_3\\ (OH)_4\end{matrix}\right](OAc)_2$, $\left[Cr_3\begin{matrix}(OAc)_3\\ (OH)_5\end{matrix}\right]OAc,28H_2O$, or by adding ammonium carbonate to the mother liquor from the penta-aceto-salt, and then removing ammonia by means of acetic acid. One part requires 1016 parts of cold water for solution. Methyl alcohol removes $16H_2O$, and a hydrate with $16H_2O$ also exists. A tri-, tetra-, and hexa-acetate have been prepared, as well as a sulphate-acetate and an ammonia compound. The salts of this series are reddish-violet.

A table of the known chromiacetates is given, and attention is

drawn to the number of isomeric salts, isomerism not having been observed in the acetates of other metals. C. H. D.

Carbohydrate Esters of the Higher Fatty Acids. III. Mannitol Esters of Lauric Acids. W. R. BLOOR (*J. Biol. Chem.*, 1912, 11, 421—428).—*Mannitan dilaurate*, $C_6H_{10}O_3(CO_2{\cdot}C_{11}H_{23})_2$, prepared by dissolving mannitol in warm concentrated sulphuric acid and adding lauric acid, forms microscopic needles, m. p. 122°. In chloroform solution, $[\alpha]_D^{20}+8{\cdot}5°$.

iso*Mannide dilaurate* was prepared by heating the preceding ester at 200° for a short time; it is colourless, has m. p. 37·5°, n_D^{40} 1·4570; $[\alpha]_D+125°$ in ether or benzene solution.

The *iso*mannide esters of lauric and closely related fatty acids are as well utilised by the animal organism as ordinary fats. W. D. H.

Fatty Acids. S. FACHINI and W. DORTA (*Chem. Rev. Fett. Harz-Ind.*, 1912, 19, 77—79. Compare *Ann. Soc. Chim. Ital. Sez. Roma*, 1910).—An account of further experiments based on an attempt qualitatively to separate mixtures of liquid and solid fatty acids by means of acetone.

The alkali salts of the higher fatty acids are practically insoluble in cold pure dry acetone; 100 c.c. of boiling 80% acetone dissolves about one gram each of sodium palmitate and sodium stearate, whilst sodium myristate is somewhat more soluble; the salts do not crystallise out, but the mixture solidifies to a clear transparent mass.

Potassium stearate is insoluble in cold 90% acetone; potassium palmitate is slightly soluble; when a mixture (1 gram) is boiled with 100 c.c. of 90% acetone, the potassium stearate crystallises out at 46°, the potassium palmitate at 28—30°, whilst any potassium myristate remains in solution. F. M. G. M.

Preparation of an Ester from Montana Wax. ERNST SCHLIEMANN'S EXPORT-CERESIN-FABRIK (D.R.-P. 244786. Compare Abstr., 1902, i, 72; 1909, i, 629; Trans., 1911, 99, 2302).—When refined Montana wax (100 parts) containing about 70% free montanic acid ($C_{28}H_{57}{\cdot}CO_2H$) and glycerol (25 parts) are heated together (preferably under pressure), an *ester* containing two molecules of acid to one of glycerol is formed; it is a colourless wax, m. p. 80—81°, and is soluble in the ordinary wax solvents. F. M. G. M.

The Colouring Matters and Nitrogenous Substances in Fats. GEORGES BOUCHARD (*Compt. rend.*, 1912, 154, 1620—1622). —The yellowish-brown aqueous layer obtained after removal of the upper layer of soap from the hydrolysis of any fatty matter by sodium hydroxide, on neutralisation gives a brown, gelatinous precipitate. This is purified by treatment with hydrochloric acid and then light petroleum; ether then extracts a soluble portion of composition approximating to $C_{18}H_{28}O_4$, the chemical behaviour of which indicates that it is a ketonic acid. The insoluble residue is a black, varnish-like mass which appears to be a mixture of acids richer in oxygen than the above mentioned, together with an acidic nitrogen

compound; the percentage of nitrogen in the latter varies from 0·5 to 3·8 with the different fats examined.

On examining more than one hundred purified fats, it was discovered that they all contained some hundredths of a % of nitrogen, the amount being as high as 0·05% for some animal fats, and as low as 0·01% for some vegetable oils. D. F. T.

Toxicity of Paints. EDWARD C. C. BALY (*J. Soc. Chem. Ind.*, 1912, 31, 515—518)—Poisonous, volatile compounds are produced somewhat readily by the action of white lead, and more readily by the action of lead hydroxide, red lead, lead peroxide, and manganese dioxide on linseed oil. On the other hand, these compounds are formed only in minute quantities at the ordinary temperature by the interaction of linseed oil and zinc white or basic lead sulphate.

The vapour evolved by a mixture of linseed oil and white lead, as already stated, is very poisonous, producing certain specific symptoms, such as lassitude and severe localised headache, followed by diarrhœa, and it is this vapour which is undoubtedly responsible for the cases of supposed lead poisoning incurred by persons who have lived in rooms freshly painted with white lead. The vapour does not contain lead, however, but is probably a mixture of unsaturated aldehydes. W. H. G.

Synthesis of Closed Rings by means of Cyanamide. 1. Cyanamide and Ethyl Acetoacetate. PERCI BRIGL (*Ber.*, 1912, 45, 1557—1563).—Ethyl acetoacetate and cyanamide condense in presence of sodium ethoxide to form the monosodium salt of *ethyl β-cyanoaminocrotonate*, $CN \cdot NH \cdot CMe\colon CH \cdot CO_2Et$. This is readily broken down into its components by acids, and contains a hydrogen atom replacable by metal. With hydrogen sulphide, an additive product, *ethyl β-thiocarbamidocrotonate*, $NH_2 \cdot CS \cdot NH \cdot CMe\colon CH \cdot CO_2Et$, is obtained. This is stable and soluble in ether, and differs from the compound obtained by List (Abstr., 1886, 443; 1887, 127) from thiocarbamide and ethyl acetoacetate, which probably contains a molecule of water more.

Sodium methoxide converts ethyl thiocarbamidocrotonate into thiomethyluracil, $CMe{<}{\begin{smallmatrix}CH \cdot CO\\ NH \cdot CS\end{smallmatrix}}{>}NH$, already described by List (*loc. cit.*).

Ethyl β-cyanoaminocrotonate forms long, asbestos-like, colourless needles, m. p. 70—72°; the *copper* salt is yellow; the *cobalt* salt is violet, subsequently becoming red; the other metallic salts are not characteristic.

Ethyl β-thiocarbamidocrotonate crystallises in yellow needles, m. p. 165—166° after previous sintering. E. F. A.

Dimorphism of Oleic Acid. AAGE KIRSCHNER (*Zeitsch. physikal. Chem.*, 1912, 79, 759—761).—A second form of oleic acid was obtained in small, white crystals on setting aside a fairly pure specimen of the acid in a flat dish at 8—10°. The new form melts at a higher temperature than the ordinary modification, but the exact melting point cannot be given, as neither the new modification or oleic acid itself has been obtained pure. G. S.

New Isomerides of Oleic Acid: $CH_3\cdot[CH_2]_4\cdot CH\colon CH\cdot[CH_2]_{10}\cdot CO_2H$ and $CH_3\cdot[CH_2]_5\cdot CH\colon CH\cdot[CH_2]_9\cdot CO_2H$. Influence of Displacement of the Double Linking in the Molecule. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 653—661).—Reduction of ricinoleic acid with hydrogen in presence of platinous hydroxide gave λ-hydroxystearic acid, which was then treated with hydrobromic acid, and the resulting bromostearic acid boiled with alcoholic potassium hydroxide, a solid and a liquid product being thus obtained.

The solid product contained stearic acid and a crystalline *Δ^λ-oleic acid*, $CH_3\cdot[CH_2]_4\cdot CH\colon CH\cdot[CH_2]_{10}\cdot CO_2H$, m. p. 34—36°, solidifying pt. 36—38°, iodine number 89·3 (theoretical 90), which on reduction by hydrogen in presence of platinous hydroxide gives stearic acid and, on oxidation with alkaline permanganate, (1) an acid, $C_5H_{11}\cdot CO_2H$; (2) a decamethylenedicarboxylic acid, $C_{12}H_{22}O_4$, m. p. 104—105·5°, solidifying pt. 92—90°; (3) λμ-dihydroxystearic acid, m. p. 85—88°, solidifying pt. 84—82°, and (4) a waxy portion, m. p. 30—40°, which is probably a glycidic acid or a ketohydroxy-acid.

The liquid product has an iodine number of about 83·8, solidifies at about 6—8°, and gives stearic acid on reduction with hydrogen in presence of platinous hydroxide, whilst on oxidation it yields (1) *n*-heptoic acid, $C_7H_{14}O_2$; (2) a dibasic acid (? nonamethylenedicarboxylic acid), $C_{11}H_{20}O_4$, m. p. 100—101°, solidifying pt. 88—85°; (3) κλ-dihydroxystearic acid; (4) a waxy product resembling that found in the solid portion. There is hence little doubt that the liquid product is Δ^κ-oleic acid.

From these results and those of other investigators, it seems that oleic acids with the double linking in an odd-even position (ηθ, ικ, λμ) are solid, whilst those with this linking in an even-odd position (θικλ) are liquid. T. H. P.

Preparation of Aluminium Glycollate. HEINRICH BYK (D.R.-P. 245490).—*Aluminium glycollate*, $Al(OH)(O\cdot CO\cdot CH_2\cdot OH)_2$, is readily prepared in crystalline form by treating an aqueous suspension of freshly precipitated aluminium hydroxide (1 mol.) with glycollic acid (2 mols.); the solution is filtered, and evaporated at 50—60° in a vacuum. F. M. G. M.

Action of Hydrogen Peroxide on Lactic Acid and on Dextrose. JEAN EFFRONT (*Compt. rend.*, 1912, **154**, 1296—1298).—Hydrogen peroxide acts on lactic acid at the boiling point of water with the formation of nearly the theoretical quantity of acetic acid. From 1—1·5% of ethyl alcohol are also obtained, and it is considered that the lactic acid has been broken down to carbon dioxide and alcohol, and the latter oxidised to acetic acid.

From dextrose under similar conditions, from 1—9% of alcohol, also acetaldehyde and acetic and formic acids are obtained in the proportion of two (acetic acid) to eight (formic acid). At the moment when the dextrose is half destroyed, 60% of volatile acids and 29% of oxalic acid are formed; when 90% of the sugar has been attacked, the proportion of oxalic acid is reduced to 7%, and when action is complete no oxalic acid is obtained. The proportion of volatile acid remains constant throughout. E. F. A.

Syntheses by means of Mixed Organic Derivatives of Zinc: α-Alkyloxyalkylacetic Acids. EDMOND E. BLAISE and L. PICARD (*Bull. Soc. chim.*, 1912, [iv], 11, 537—546. Compare Abstr., 1911, i, 349; this vol., i, 232).—The production of ethyl chloroethoxyacetate and its reaction with mixed organic compounds of zinc, already dealt with (*loc. cit.*, compare Mylo, this vol., i, 4), are described in greater detail. The latter reaction is of special interest, since it is a general method for the synthesis of α-alcohols by the direct attachment of the group $-CH(OH)\cdot CO_2H$ to any radicle.

Ethyl α-ethoxy-*n*-valerate, b. p. 84°/17 mm. or 76°/12·5 mm., obtained as already described (*loc. cit.*) or by treating α-bromovaleryl chloride with ethyl alcohol, forms on hydrolysis *α-ethoxyvaleric acid*, b. p. 114°/11 mm., 124°/17 mm., as as slightly viscous liquid. The *methyl* ester, b. p. 70°/15 mm., is a mobile liquid; the acid *chloride*, b. p. 57—58°/12·5 mm., is liquid; the *amide*, m. p. 91°, forms colourless needles. The *anilide*, m. p. 68°, crystallises from a mixture of benzene and light petroleum. The p-*toluidide*, b. p. 184°/11·5 mm., is liquid.

T. A. H.

Uranyl Oxalate. WILLIAM OECHSNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1912, [iv], 11, 531—533).—Uranyl oxalate, $UO_2C_2O_4$, is moderately soluble in water, and sparingly soluble in alcohol (95°) or dry methyl alcohol, becomes anhydrous at 100°, and then on exposure to moist air, slowly absorbs $3H_2O$. On ignition in a closed vessel, it leaves a residue of uranous oxide, UO_2, in a condensed form, which is black, but shows green or brown tints by reflected light.

T. A. H.

The Esters of Dichlorosuccinic Acid and Their Stereoisomerides. GEORGES DARZENS and J. SÉJOURNÉ (*Compt. rend.*, 1912, 154, 1615—1617).—Two inactive dichlorosuccinic acids have already been described (Kirchhoff, Abstr., 1895, i, 20; Michael and Tissot, Abstr., 1893, i, 142; Riet, Abstr., 1895, i, 19).

On treating methyl *d*-tartrate in pyridine solution with thionyl chloride there is obtained an active *methyl dichlorosuccinate*, b. p. 126°/20 mm., 106°/4 mm., m. p. 62—63°, $[\alpha]^{20}$ − 66° (in chloroform).

The corresponding *ethyl dichlorosuccinate*, obtained in a similar manner from ethyl *d*-tartrate, has b. p. 116°/3 mm., and does not crystallise.

Methyl *dl*-tartrate under similar treatment yields an inactive product, presumably *methyl* dl-*dichlorosuccinate*, b. p. 105°/3 mm., m. p. 43°; this differs from both the inactive esters previously described (*loc. cit.*), and appears to offer a case of isomerism somewhat analogous to that of the malic acids.

Contrary to expectation, all the above esters on elimination of hydrogen chloride give ethyl chlorofumarate, b. p. 117°/7 mm. This is explained by an assumption that the elimination of hydrogen chloride occurs at one carbon atom, and is followed by the movement of a hydrogen atom from the other carbon. The chlorofumaric esters resist the elimination of another molecule of hydrogen chloride.

D. F. T.

The Decomposition of Some Higher Acids of the Oxalic Acid Group by Heat. OSSIAN ASCHAN (*Ber.*, 1912, **45**, 1603—1609).—Adipic, suberic, and sebacic acids, when submitted to dry distillation, are found to undergo changes in three directions: I, elimination of carbon dioxide and water, resulting in *cyclo*ketones; II, loss of carbon dioxide alone, giving saturated mono-basic acids; and III, the formation of unsaturated monobasic acids.

From adipic acid, *cyclo*pentanone has been obtained in 60% yield, whilst valeric acid has been characterised in the form of its calcium salt, and potassium permanganate has revealed the presence of an unsaturated acid. Suberic and sebacic acids are more liable to complete decomposition, and the formation of ketones occurs to a much smaller extent, whilst larger yields of saturated and unsaturated acids are obtained. The formation of suberone and *n*-heptoic acid in the one case, and of *cyclo*nonanone and *n*-nonoic acid in the other, has been proved. J. C. W.

Preparation of αβ-Diketonic Esters. ANDRÉ WAHL and M. DOLL (*Compt. rend.*, 1912, **154**, 1237—1240).—The preparation, properties, and certain reactions of homologues of ethyl acetylglyoxalate (ethyl diketobutyrate) are described (compare Bouveault and Wahl, Abstr., 1904, i, 556; Wahl, Abstr., 1907, i, 217; 1911, i, 108). The new esters were prepared by the general method already described.

Ethyl propionylglyoxalate, $CH_2Me\cdot CO\cdot CO\cdot CO_2Et$, b. p. 77—80°/10 mm., D^0 1·142, is sparingly soluble in water. *Ethyl butyrylglyoxalate* has b. p. 83—86°/10 mm., D^0 1·104. *Ethyl heptylglyoxalate*, b. p. 124—128°/10 mm., D^0 1·021, is insoluble in water. All these esters are pleasant-smelling, mobile, yellow liquids, which are decolorised by water or alcohol; with aniline and hydroxylamine they yield uncrystallisable oils. With *o*-diamines they furnish quinoxaline derivatives; thus ethyl propionylglyoxalate gives with *o*-phenylenediamine, *ethyl 2-ethylquinoxaline-3-carboxylate*, colourless needles, m. p. 64°. With 1:2-naphthylenediamine, ethyl heptylglyoxalate yields *ethyl 2-hexylphenoquinoxaline-3-carboxylate*, m. p. 64—65°, whilst the corresponding *compound* given by ethyl butyrylglyoxalate has m. p. 83—84°.

The *disemicarbazones* derived from the three homologous diketonic esters in ascending order melt with decomposition at 235°, 247°, and 230° respectively, and are colourless, crystalline, sparingly soluble substances.

With phenylhydrazine, ethyl propionylglyoxalate yields *1-phenyl-3-ethyl-5-pyrazolone-4-phenylhydrazone*, $C_6H_5\cdot N<\begin{matrix} N{=}CEt \\ CO{-}C{:}N\cdot NHPh \end{matrix}$, orange crystals, m. p. 157°. The corresponding *compounds* formed from the other two esters in ascending order have m. p. 133—134° and m. p. 100—101° respectively (compare Bouveault and Wahl, Abstr., 1904, i, 789).

With hydrazine hydrate the esters form the corresponding rubazonic acids of the type already described by Bouveault and Wahl (*loc. cit.*).

3 : 3′-*Diethylrubazonic acid*, $NH\langle{}^{CO\cdot CH\cdot N:C-CO}_{N=CEt\quad CEt:N}\rangle NH$, m. p. 235° (decomp.), and the corresponding *dipropylrubazonic acid*, m. p. 260° (approx.), both form red crystals and give violet tinted solutions with alkalis. T. A. H.

Preparation of the Unconjugated Acids of Ox Bile. Samuel B. Schryver (*J. Physiol.*, 1912, **44**, 265—274).—The crude acids are recrystallised from hot acetone, and over 80% are obtained in crystalline form. From the mixture the greater part of the cholic acid can be separated by heating a 1% solution of the sodium salts with one-fifth the volume of a 20% magnesium chloride solution on a water-bath. Most of the choleic and deoxycholeic acids separate as the magnesium salt, and the greater part of the cholate remains in solution. From the mixture of choleate and deoxycholeate, the former can be separated as an insoluble barium salt, and the deoxycholeic acid can be separated from the greater part of the still adhering cholic acid by reconversion into the magnesium salt. No trace of Hans Fischer's lithocholic acid was found; it is possibly a pathological product. W. D. H.

Preparation of α-Glucoheptonic Acid. Arthur Liebrecht and Georg Rosenfeld (D.R.-P. 245267).—α-Glucoheptonic acid is obtained in satisfactory yield when the product obtained from the treatment of dextrose during six days with hydrogen cyanide at 30° is boiled with barium hydroxide, the resulting precipitate decomposed with sulphuric acid, and the filtrate evaporated in a vacuum. F. M. G. M.

Use of Carbonates in the Catalytic Preparation of Ketones. Jean B. Senderens (*Compt. rend.*, 1912, **154**, 1518—1520).—A claim that his process for the preparation of ketones directly from acids, using thorium, zirconium, or uranium oxides as catalysts (compare Abstr., 1909, i, 286, 627; 1910, i, 11, 179, 318, 489; 1911, i, 134, 302) is independent of the work of Squibb and Conroy, who used carbonates. Further, the author points out that carbonates which, like many other compounds, furnish good yields of acetone from acetic acid, are almost inactive or produce irregular results with the homologues of this acid. W. G.

Chemical Action of Light. XXIII. Behaviour of Methyl Ethyl Ketone. Giacomo L. Ciamician and Paul Silber (*Ber.*, 1912, **45**, 1540—1546*).—It has been shown (Abstr., 1911, i, 513) that methyl ethyl ketone in methyl and ethyl alcoholic solution behaves very differently from acetone when exposed to light. In the case of acetone, *iso*butylene glycol and trimethylethylene glycol are formed; with methyl ethyl ketone no glycol could be identified. It is now established that methyl ethyl ketone condenses with itself to form a diketone, $C_8H_{14}O_2$, the other product of the reaction being

* and *Atti R. Accad. Lincei*, 1912, [v], **21**, i, 547—553.

sec.-butyl alcohol. This diketone reacts with ammonia to form tetramethylpyrrole; it accordingly has the structure

COMe·CHMe·CHMe·COMe.

The higher ketones behave similarly, whilst the products of the action of light on acetone when heated with ammonium acetate give a faint, but distinct, pine-splinter reaction for pyrrole, and also the Ehrlich reaction for acetonylacetone.

The *diketone*, $C_8H_{14}O_2$, has b. p. 82°/11 mm.; it forms a *dioxime*, crystallising in large, lustrous prisms, m. p. 202°.

The tetramethylpyrrole formed from it separates in nacreous platelets, m. p. 114°; the *picrate* has yellow, prismatic crystals, m. p. 130°; the *compound* with trinitroresorcinol forms reddish-brown needles, m. p. 159°.

The diketone reacts with phenylhydrazine to form a *pyrrole*, $C_{14}H_{18}N_2$, crystallising in colourless needles, m. p. 130°.

With *p*-phenylenediamine, a *compound* of the same composition, separating in faintly coloured, prismatic crystals, m. p. 174—175°, is obtained. E. F. A.

The Preparation of Glucosone. Paul Meyer (*Biochem. Zeitsch.*, 1912, 40, 455—457).—In view of the fact that glucosazone is not soluble in water, the ordinary method of preparing glucosone from this by treatment with benzaldehyde has failed. The author shows, however, that glucosazone is soluble in benzaldehyde, and if 2 grams of the osazone are dissolved in 18 grams of the aldehyde and the mixture heated with 200 c.c. of water, glucosone is obtained in a yield up to 30% of the theoretical. S. B. S.

Action of Ultra-violet Rays on Starch. Jean Bielecki and René Wurmser (*Compt. rend.*, 1912, 154, 1429—1432. Compare Abstr., 1910, i, 625; 1911, i, 255, 524).—Pure starch in aqueous solution when exposed to the ultra-violet rays from a quartz-mercury lamp undergoes hydrolysis and partial oxidation. The products formed are dextrins, reducing sugars (probably dextrose), pentoses, formaldehyde, and substances of an acid nature. W. G.

Action of Ultra-violet Rays on Starch. Léon Massol (*Compt. rend.*, 1912, 154, 1645—1646. Compare Massol, Abstr., 1911, i, 356; Bielecki and Wurmser, preceding abstract).—A claim for priority. D. F. T.

Hydrolysis of Starch by Hydrogen Peroxide, alone or in the Presence of Animal and Vegetable Amylases. C. Gerber (*Compt. rend.*, 1912, 154, 1543—1545).—Hydrogen peroxide even in dilute solutions (1 part perhydrol in 1000—3000 water) has a powerful hydrolysing effect on starch, the products being maltose and dextrins. In more concentrated solutions, oxidation of the maltose occurs. This hydrolysis is more closely allied to diastatic action than is the case with acids, maltose and not dextrose being the sugar formed. Rise in temperature increases the rate of the reaction very considerably.

A solution of perhydrol (1 : 8000) has a powerful retarding influence

on the amylase of *Ficus carica*, but has no effect on that of *Broussonetia papyrifera*, a strength of 1 : 25 being necessary to cause retardation with this amylase. With the amylase of trypsin, a solution 1 : 1000 has a slight accelerating effect, whilst a solution 1 : 25 has a marked retarding influence. W. G.

Acid of Oxalic Acid on Cellulose. Cellulose-oxalic Acid Ester. JOHN F. BRIGGS (*J. Soc. Chem. Ind.*, 1912, 31, 520—522).—Cellulose is converted by oxalic acid, slowly at the ordinary temperature, more rapidly at higher temperatures, partly into a hydrocellulose and partly into a compound which is probably an acid oxalate of a hydrocellulose. The ester has not yet been isolated; it exhibits, even in the form of a sodium salt, a strong affinity for basic dyes.

W. H. G.

Physical and Chemical Properties of Some Organic Amalgams. HERBERT N. McCOY and FRANKLIN L. WEST (*J. Physical Chem.*, 1912, 16, 261—286. Compare McCoy and Moore, Abstr., 1911, i, 270).—The method of preparing tetramethylammonium amalgam previously described has been improved by carrying out the electrolysis of alcoholic tetramethylammonium chloride in a vessel cooled to $-34°$ by liquid ammonia. The electrolytic efficiency of the process was about 15% with ethyl alcohol and somewhat higher with propyl alcohol and acetonitrile as electrolytes.

The amalgam was filtered by suction from the excess of liquid mercury, and the silver-white, granular, crystalline amalgam, having been washed with carbon tetrachloride, could be preserved under carbon tetrachloride at 0° for several hours. The crystals contained upwards of 5% of their mercury in combination, as estimated from the proportion of colloidal mercury obtained when water was added. The crystals float on liquid mercury, densities as low as 10·6 being recorded. The electrical conductivity falls off as the percentage of amalgam increases.

Tetramethylammonium amalgam spontaneously emits negative electricity as it decomposes, and the residual amalgam, if insulated, acquires a positive charge, attaining in one case 3·8 volts in a few minutes. A positively charged electroscope is discharged by the emission at a rate which is greater the higher the temperature of the amalgam and the nearer it is to the electroscope. The emission is without effect on a photographic plate, and is unable to pass through 0·044 mm. of aluminium, but may be carried by a current of air through a layer of glass wool or a long narrow tube. The conclusion is drawn that the phenomenon is not one of radioactivity, but consists of the emission of ionised molecules of the gaseous decomposition products.

Ammonium amalgam emits positive electricity as observed by Coehn, and also negative in about 1/50th to 1/20th the amount. Monomethylammonium amalgam also gives both kinds of ion, the proportions being similar. Tetramethylammonium amalgam is peculiar in that it emits no positive ions. The gas escaping from the mercury in minute bubbles is negatively electrified just as in the case

of air bubbled through mercury, as noticed by Lenard (1892). The phenomenon is distinct from that shown by potassium and sodium amalgams, in that ultra-violet light is not necessary, and, in fact, has no appreciable influence.

The decomposition of tetramethylammonium amalgam at 25° appears to take place according to the equation:

$$4Hg_x(CH_3)_4N \longrightarrow 4(CH_3)_3N + 2CH_4 + C_2H_4 + xHg,$$

although the authors consider that this is not definitely established. The rate at which gas is evolved at 27° indicates that the action is unimolecular, so that it is necessary to assume that it takes place in stages. It is calculated that only one ion is produced per 10^{10} molecules of trimethylamine evolved.

The preparation of monomethylammonium amalgam was also investigated. It was found that there is no better electrolyte than water in this case, and there is no advantage in working at −34° instead of 0°. R. J. C.

Precipitating Reagents for Amino-acids. CARL NEUBERG and JOHANNES KERB (*Biochem. Zeitsch.*, 1912, **40**, 498—512).—Mercuric acetate precipitates amino-acids in the presence of carbonates. The mercuric salts are not the normal salts of the acids, but appear to be the salts of the carbamic acids, formed by the action of the carbonate on the amino-acids; thus glycine, for example, appears to react as follows: $CO_2H\cdot CH_2\cdot NH_2 + Na_2CO_3 = CO_2Na\cdot CH_2\cdot NH\cdot CO_2Na$. Mercuric acetate acting on compounds of this description gives rise to basic mercuric salts of the corresponding acid; the reasons for these suppositions are the following: (1) The normal mercuric salts of amino-acids which are known have different properties to those obtained in the above reaction, some of them being easily soluble. (2) Glucosamine which contains no carboxyl group also gives a precipitate when treated with sodium carbonate and mercuric acetate. (3) Sodium carbonate is essential for the reaction, and cannot be replaced by sodium hydroxide. (4) On decomposition of the salts with hydrogen sulphide, carbon dioxide is evolved. (5) Similar precipitates could be obtained directly from the corresponding carbamic acids prepared by Siegfried's method. The authors give full details for carrying out the reaction. S. B. S.

Creatinine. ERNST SCHMIDT (*Apoth. Zeit.*, 1912, Reprint 3 pp. Compare Abstr., 1911, i, 20).—The product obtained by the action of sodium nitrite on a nitric acid solution of creatinine is not a nitroso-compound, but an oxime; on treatment with hydrochloric acid, it gives hydroxylamine and an acidic substance, which proves to be methylparabanic acid, so that its constitution probably is $CO{<}\begin{matrix}NMe\cdot C{:}N\cdot OH\\ NH{-}CO\end{matrix}$, that is, the *oxime* of *methylparabanic acid.*

The "nitrosocreatinine" of Kramm (Abstr., 1899, i, 85), obtained by the action of sodium nitroprusside on creatinine, is probably the guanidine analogue, $NH{:}C{<}\begin{matrix}NMe\cdot C{:}N\cdot OH\\ NH{-}CO\end{matrix}$. Unlike the above

oxime, it possesses basic properties. On hydrolysis with hydrochloric acid, it yields, amongst other products, hydroxylamine and methylparabanic acid; on reduction with tin and hydrochloric acid, it gives a considerable quantity of methylguanidine. D. F. T.

Oxidation of Potassium Cyanate by means of Hydrogen Peroxide. ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 527—528. Compare Abstr., 1911, i, 429, 618).—In neutral solution the reaction between potassium cyanate and hydrogen peroxide seems to proceed according to the equation: $2KCNO + H_2O_2 = K_2CNO_2 + CNO + H_2O$. Not only the gas from the salt remaining in solution, but also that evolved, which is mainly soluble in alkali hydroxide and gives a precipitate with barium hydroxide solution, possesses a less weight than carbon dioxide. In presence of sodium hydroxide, which must be free from carbonate, the reaction is expressed by the equation: $2KCNO + 2NaOH + 2H_2O_2 = K_2CNO_2 + Na_2CNO_2 + 2H_2O$. Also, in presence of concentrated alcohol, which annuls the hydrolysing action of the water, the oxidation proceeds without generation of gas. T. H. P.

Formation of Oxycyanates on Heating Potassium Cyanate with Copper Oxide or on Combustion of Potassium Cyanate in Oxygen. ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 529—532. Compare preceding abstract).—When potassium cyanate is heated with a small quantity of an oxide or of a finely divided metal, for example, copper, it undergoes energetic oxidation according to the equations: $2KCNO + CuO = K_2CNO_2 + CNO + Cu$ and $2KCNO + Cu = K_2CNO_2 + CN + Cu$. The quantities of gas evolved do not correspond exactly with these equations, owing to secondary reactions occurring to a slight extent. T. H. P.

Synthesis of Carbamide by the Oxidation of Ammonia and Carbohydrates, Glycerol, or Formaldehyde. ROBERT FOSSE (*Compt. Rend.*, 1912, **154**, 1448—1450).—Contrary to the statement of Hofmeister (Abstr., 1897, ii, 335), carbamide is formed in considerable quantities when dextrose, lævulose, sucrose, dextrin, inulin, starch, glycerol or formaldehyde are oxidised in the presence of ammonium salts by means of potassium permanganate. The permanganate is added slowly to the ammoniacal sugar solution, and the mixture is then heated at 50—60° until the permanganate is all destroyed. After the addition of acetic acid, the liquid is filtered and the carbamide is precipitated by the addition of an alcoholic solution of xanth-hydrol. W. G.

Preparation of Carbamic Esters of Tertiary Alcohols. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 245491).—The carbamic esters of tertiary alcohols are readily prepared by the action of a metal on a mixture of the alcohol and carbamyl chloride. *Amylene carbamate*, $NH_2 \cdot CO_2 \cdot C_5H_{11}$, colourless needles, m. p. 83—86°, with a camphor-like odour was prepared by treating a cooled mixture of amylene hydrate (88 parts), benzene (600 parts), and sodium (23 parts)

with carbamyl chloride (79·5 parts); the solution was acidified, filtered, the benzene removed by distillation, and the oily residue crystallised from alcohol. This reaction can also be carried out by Grignard's method.

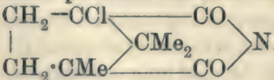
Methyldiethylcarbinylurethane, colourless needles with a camphor-like odour, was obtained by adding methyl ethyl ketone (1 mol.) to magnesium ethyl chloride (prepared by Grignard's reaction), followed when the action moderated by carbamyl chloride to the well cooled solution. F. M. G. M.

Addition of Ethylidenebisurethane to Acetylacetone. II. G. Bianchi (*Gazzetta*, 1912, **42**, i, 499—502).—Replacement of the aromatic aldehyde previously employed (Abstr., 1911, i, 977) by acetaldehyde shows that alkylidene-urethanes, as well as arylalkylidene-urethanes give the additive reaction with β-carbonyl compounds.

Urethanoethylideneacetylacetone, $CHAc_2\cdot CHMe\cdot NH\cdot CO_2Et$, prepared by the interaction of acetylacetone, urethane, and acetaldehyde (the last two compounds first reacting to give ethylidenebisurethane), forms radiating masses of white needles, m. p. 77°, gives the normal molecular weight in boiling benzene, exhibits neither acid nor basic reaction, and is highly stable towards mineral acids. T. H. P.

Chlorocamphornitrilic Acid. Johann Scheiber and Max Knothe (*Ber.*, 1912, **45**, 1551—1553. Compare Bredt, this vol., i, 411).—Camphornitrilic acid is converted by aqueous sodium carbonate into camphanonitrile and camphanamide. Hydrogen cyanide is also produced, but camphonic acid could not be detected.

Chlorocamphornitrilic acid when placed in a bath at 180—190° melts, becoming solid again on continued heating with the appearance of melting at 240°, followed by decomposition. When heated slowly, beginning at the ordinary temperature, it sinters at 170°. The product formed on heating at 200° is *chlorocamphorimide*,



which crystallises in needles or platelets, decomp. above 280°. This is also obtained from chlorocamphor-nitrilic acid on treatment with concentrated hot hydrochloric acid. E. F. A.

Carbon Pernitride. Georges Darzens (*Compt. rend.*, 1912, **154**, 1232—1234).—The formation and properties of carbon pernitride are described.

Carbon pernitride, $N{:}C\cdot N<\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}$ or $N{:}C\cdot N{:}N{:}N$, m. p. 35·5—36°, formed by the action of cyanogen bromide on a well-cooled solution of sodium azoimide in water, forms colourless, odourless needles, soluble in water, alcohol, ether, or benzene, sparingly soluble in light petroleum. It sublimes slightly above its m. p. in a vacuum, but at 70° begins to decompose, and between 170° and 180° explodes with great violence. It is particularly sensitive to shock, and should only be prepared in small quantities. It is stable when pure, but in

presence of traces of bromine passes into a polymeride insoluble in ether; in aqueous solution it undergoes hydrolysis, furnishing eventually azoimide and carbon dioxide. Its heat of formation determined in a calorimetric bomb was $-92 \cdot 6$ cal., and that of the polymeride, $-82 \cdot 2$ cal. T. A. H.

The Composition of Potassium Ferrocyanide Gold-Baths. Ernst Beutel (*Zeitsch. angew. Chem.*, 1912, **25**, 995—998).—Potassium ferrocyanide gold-plating baths always contain alkali (sodium or potassium carbonate) to prevent the formation of Prussian-blue. Having previously studied the reaction between chlorauric acid and potassium ferrocyanide (Abstr., 1910, i, 723), the author has now investigated the effect of the addition of potassium carbonate in order to account for the phenomena observed with the above-mentioned bath. The action which takes place when the solution is boiled for a long time, oxygen being blown through the solution at intervals, is represented quantitatively by the equation: $14HAuCl_4 + 10K_4FeC_6N_6 + 15K_2CO_3 + 5O + 10H_2O = 14KAuC_4N_4 + 56KCl + 4HCN + 15CO_2 + 10Fe(OH)_3$. If the ferrocyanide is in excess, the following reaction takes place, some ferricyanide being formed: $14HAuCl_4 + 14K_4FeC_6N_6 + 13K_2CO_3 + 7O + 10H_2O = 14KAuC_4N_4 + 56KCl + 4HCN + 13CO_2 + 10Fe(OH)_3 + 4K_3FeC_6N_6$. In both these reactions the formation of the potassium auricyanide takes place slowly, and prolonged boiling is necessary.

The above results show that the ferrocyanide plating-bath is really one of potassium auricyanide. The fiery, yellowish-green colour which it possesses is not due to the presence of gold, as has usually been supposed to be the case, but to the presence of potassium ferricyanide. T. S. P.

Reduction of Ethyl Diazoacetate. August Darapsky and Moreshwar Prabhakar (*Ber.*, 1912, **45**, 1654—1665).—It was found previously that ethyl hydrazinophenylacetate is converted by nitrous acid into ethyl nitrosohydrazinophenylacetate, and this by sulphuric acid into ethyl triazophenylacetate (Darapsky, *Zeitsch. angew. Chem.*, 1910, **23**, 2320), whereas Traube and Hoffa (Abstr., 1898, i, 235) found that ethyl hydrazinoacetate gave ethyl diazoacetate. The present paper describes better methods for the production of this ester, which forms a well-defined hydrochloride, and shows that the expected analogy with the phenylated compounds does also exist.

The hydrochloride of ethyl hydrazinoacetate is obtained in 40% yield by the interaction of hydrazine hydrate and monochloroacetic acid in alcohol, but a still better process, giving 90% yields, is the reduction of ethyl diazoacetate by means of sodium amalgam. Energetic reduction of this substance yields glycine, whilst ferrous sulphate produces the unstable ethyl hydraziacetate, the presence of this intermediate stage being also shown in the present process. The authors suggest that these reactions are best explained by adopting the open diazonium formula of Angeli and J. Thiele (Abstr., 1911, i, 845; 1912, i, 16) for fatty diazo-compounds. Hydraziacetic acid is therefore the

hydrazone of glyoxylic acid, which further reduction converts into the corresponding hydrazine:

$N{\vdots}N{:}CH{\cdot}CO_2H \xrightarrow{+H_2} NH_2{\cdot}N{:}CH{\cdot}CO_2H \xrightarrow{+H_2} NH_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H.$

An analogous case is the reduction of diazomethane to methylhydrazine (Pechmann, Abstr., 1895, i, 328). The free hydrazinoacetic acid (compare Traube and Hoffa, *loc. cit.*) may be obtained from the ester by means of baryta.

When the ester is treated with two molecules of nitrous acid, it breaks down into ethyl diazoacetate, a reaction which recalls the formation of a benzenediazonium salt by the action of nitrous acid on phenylhydrazine (Thiele, Abstr., 1908, i, 927). Curtius and Jay (Abstr., 1889, 340), by the reduction of ethyl diazoacetate with zinc and acetic acid, also obtained what are now regarded as indications of the formation of ethyl hydrazinoacetate, which shows another analogy between fatty and aromatic diazo-compounds, being comparable with E. Fischer's reduction of diazobenzene to phenylhydrazine.

When the hydrochloride of ethyl hydrazinoacetate is treated with one molecular proportion of sodium nitrite, the intermediate *ethyl nitrosohydrazinoacetate*, $NH_2{\cdot}N(NO){\cdot}CH_2{\cdot}CO_2Et$, can be extracted with ether, which does not, however, effect complete extraction, as the substance is very soluble in water. It is a faint yellow oil producing a violet colour with ferric chloride. It partly decomposes on heating under reduced pressure, completely in the air, into nitrous oxide and ethyl aminoacetate; nitrous acid converts it into ethyl diazoacetate, and dilute sulphuric acid into ethyl triazoacetate.

J. C. W.

Conversion of *cyclo*Hexane into Benzene. RICHARD WILLSTÄTTER and DAVID HATT (*Ber.*, 1912, **45**, 1464—1471).—The authors have applied the method of fission of ammonium bases at greatly reduced pressure (this vol., i, 17) to the introduction of three double bonds into *cyclo*hexane.

For the preparation of *cyclo*hexene, *cyclo*hexanol was heated with oxalic acid (Zelinsky and Zelikoff, Abstr., 1902, i, 2). The yields were unsatisfactory, owing to the formation of considerable quantities of cyclo*hexyl oxalate*, m. p. 42°. Better yields of *cyclo*hexene were obtained from *cyclo*hexanol and potassium hydrogen sulphate (compare Brunel, Abstr., 1905, i, 268), from which also small quantities of cyclo*hexyl ether*, b. p. 239—240°/727 mm., 97—98·5°/8 mm., were isolated. For some unexplained reason, the latter compound is not identical with the *cyclo*hexyl ether prepared by Ipatieff and Philipoff (Abstr., 1908, i, 342). *cyclo*Hexene was converted into its dibromide, from which, after heating with dimethylamine in benzene solution, *dimethylamino*-Δ^2-cyclo*hexene*, b. p. 160·5—162·5°/725 mm., 89—91·5°/80 mm., was prepared. Its *platinichloride*, m. p. 185° (decomp.), and *methiodide*, m. p. 173—174°, were analysed. The corresponding ammonium *base* when heated under diminished pressure yielded trimethylamine and $\Delta^{1,3}$-*cyclo*hexadiene, b. p. 78·3—78·8°/727 mm., D_4^{20} 0·8404, n_D^{20} 1·47439, n_α^{20} 1·47025, n_β^{20} 1·48516, n_γ^{20} 1·49491. In the presence of platinum, it readily absorbed two molecules of hydrogen.

An examination of *cyclo*hexadiene obtained from *cyclo*hexenedibromide and quinoline (Crossley, Trans., 1904, **85**, 1403) showed it to be contaminated with *cyclo*hexene (compare Harries and von Splawa-Neymann, Abstr., 1909, i, 218), bromo*cyclo*hexene (compare Zelinsky and Gorsky, Abstr., 1911, i, 847), and benzene.

From the product of the action of dibromo*cyclo*hexene on dimethylamine in cold benzene solution, *tetramethyldiamino*-Δ^2-cyclo*hexene*, b. p. 90·5—92·5°/10 mm., 219·5—223·5°/725 mm., D_4^0 0·920, was isolated. Its *platinichloride*, darkening at about 240°, m. p. 259—260° (decomp.), and *methiodide*, m. p. 236° (decomp.), were examined. The corresponding quaternary base yielded trimethylamine and benzene on decomposition, this occurring at 98—104°/atmospheric pressure, 40—45°/20 mm., and −3 to +5°/0·008—0·02 mm. The benzene so obtained readily absorbed three molecules of hydrogen, and was in all respects identical with ordinary pure benzene. H. W.

Hydrogenation of Aromatic Compounds by means of Platinum and Hydrogen. RICHARD WILLSTÄTTER and DANIEL HATT (*Ber.*, 1912, **45**, 1471—1481).—The quantitative hydrogenation of a variety of aromatic compounds has been studied. Full details of the method of preparing the platinum and of the arrangement of apparatus are given. In general, aromatic substances absorb hydrogen more slowly than do hydroaromatic or olefinic compounds, and hydrogenation appears to take place without the formation of intermediate compounds.

Chemically pure benzene is readily hydrogenated when dissolved in glacial acetic acid. In the absence of a solvent, it appears to possess a retarding influence on the activity of the platinum. The presence of a trace of thiophen completely inhibits absorption of hydrogen. Thiophen itself could not be hydrogenated. Commercial toluene and xylene are readily converted into methyl*cyclo*hexane and dimethyl*cyclo*hexane respectively. Durene is converted into 1 : 2 : 4 : 5-*tetramethyl*cyclo*hexane*, b. p. 169—170·5°/711 mm., D_4^0 0·825, D_4^{20} 0·811, n_C^{20} 1·44260, n_D^{20} 1·44511, n_F^{20} 1·45064, n_G^{20} 1·45524. The purest commercial naphthalene could not be hydrogenated in glacial acetic acid solution, and was found to contain 0·25% sulphur. Pure naphthalene, on the other hand, readily absorbs hydrogen in ethereal, or more rapidly in glacial acetic acid, solution, with the formation of decahydronaphthaline, b. p. 188·5—190·5°/717 mm. (compare Leroux, Abstr., 1904, i, 987). Phenol is converted into a mixture of *cyclo*hexanol and *cyclo*hexane. The reduction of aniline leads to the formation of ammonia, amino*cyclo*hexane, and di*cyclo*hexylamine, the *aurichloride* of which is described. Benzoic acid is readily reduced to *cyclo*hexanecarboxylic acid. *m*-Chlorotoluene, dissolved in glacial acetic acid, readily reacts with hydrogen, but reaction ceases after the absorption of $1\frac{1}{2}$ atoms, hydrogen chloride being simultaneously formed. The behaviour of allyl bromide is similar. Pure pyrrole is reduced to pyrrolidine in glacial acetic acid, but not in ethereal solution, whilst pyrrole which contains a trace of sulphur compounds is not so reducible. *iso*Hæmopyrrole can also be similarly hydrogenated. H. W.

Bromination of Some Hydroaromatic Compounds. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1912, **154**, 1514—1515. Compare Abstr., 1911, i, 533).—Bromine acting in the presence of aluminium bromide attacks 1-chloro-2-iodo-, 1-chloro-1 : 2-dibromo-, and 1 : 2-dichloro*cyclo*hexane and various liquid di-, tri-, and tetrachloro*cyclo*hexanes, forming in all cases hexabromobenzene. Chloro-Δ^1-*cyclo*hexene behaves in the same way towards bromine. Tetrachloro*cyclo*hexane, m. p. 173°, is, however, unacted on under the same conditions. A hydrocarbon, b. p. 80—81°, obtained by the action of quinoline on 1 : 2-dibromo*cyclo*hexane, yields hexabromobenzene when submitted to the above method of bromination. In cold chloroform solution, however, it yields a *tetrabromo*cyclo*hexane*, m. p. 85—86°. which is only slowly attacked by bromine containing 1% aluminium.

W. G.

Sulphoxide and Sulphone Groups. OSCAR HINSBERG (*J. pr. Chem.*, 1912, [ii], **85**, 337—352).—Trimethylenetrisulphoxide and diphenylsulphoxidemethane possess acid properties and yield condensation products with diazonium salts; from this the conclusion is drawn that the sulphoxide group is an ionogen of the second order (compare Abstr., 1911, ii, 873).

Trimethylenetrisulphoxide, $SO<\begin{matrix}CH_2\cdot SO\\CH_2\cdot SO\end{matrix}>CH_2$, prepared by oxidising trimethylene trisulphide with 30% hydrogen peroxide in glacial acetic acid solution, crystallises from water in colourless needles, which become brown at 235°, and have m. p. about 270° (decomp.). It decomposes explosively when rapidly heated, and is reduced by hydriodic acid or sodium hydrogen sulphite to the original trisulphide.

When warmed with alcoholic sodium ethoxide, it yields a *sodium* salt, $C_3H_5O_3S_3Na$, which forms a heavy, sandy powder and explodes at 120—130°. The sulphoxide dissolves in hydrochloric acid, forming an unstable *hydrochloride*, and condenses with benzaldehyde in the presence of sodium hydroxide, yielding an unstable, white, amorphous *substance*, m. p. 155—165° (decomp.). The *condensation products* with benzenediazonium chloride, β-naphthalenediazonium chloride, and diazotised β-naphthylamine-2 : 7-disulphonic acid are also described.

Diphenylsulphoxidemethane (*diphenylsulphinylmethane*),

$$CH_2(SO\cdot C_6H_5)_2,$$

prepared by oxidising diphenylthiolmethane with hydrogen peroxide in acetic acid solution at 0°, crystallises in prisms, m. p. 194°, and decomposes at a slightly higher temperature into diphenyl disulphide and formic acid. It dissolves in concentrated hydrochloric acid and also in alcoholic sodium ethoxide. It condenses with benzenediazonium chloride, yielding a brick-red *substance*, $C(SOPh)_2{:}N\cdot NHPh$ or $CH(SOPh)_2\cdot N{:}NPh$.

Phenylsulphoxidephenylsulphonemethane, $SO_2Ph\cdot CH_2\cdot SOPh$, is obtained by oxidising diphenylthiolmethane with 30% hydrogen peroxide and glacial acetic acid at the ordinary temperature. It forms thin, colourless prisms, m. p. 163° (decomp.).

With respect to the sulphone group, $:SO_2$, it is pointed out that this differs from the other ionogenic groups of the second order in not

exerting a reactivating influence on adjacent methylene-hydrogen atoms; thus β-disulphones possess marked acid properties, but the methylene groups are not reactive. This difference is referred by the author to the difficulty with which the sulphones pass into the *aci*-form. F. B.

Preparation of Phenyl*cyclo*hexane and Di*cyclo*hexyl; Direct Hydrogenation of Diphenyl. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1912, **154**, 1390—1392).—Eykman (Abstr., 1904, i, 26) obtained only phenyl*cyclo*hexane by direct hydrogenation of diphenyl in the presence of reduced nickel. The authors have repeated this experiment and find that this is the first step in the reduction, and that on submitting this product to further hydrogenation with a large excess of hydrogen at 160°, di*cyclo*hexyl is obtained in a nearly pure state. Phenyl*cyclo*hexane and di*cyclo*hexyl are best distinguished from one another by the action of a mixture of sulphuric and nitric acids in the cold. The former is violently attacked, giving solid nitro-compounds, whilst the latter is hardly acted on. W. G.

Passage of the Nitro-group from an Aliphatic Carbon Atom to the Benzene Nucleus. GIACOMO PONZIO (*Gazzetta*, 1912, **42**, i, 525—527).—The author has previously described two cases of intramolecular rearrangement in which the nitro-group passes from aliphatic carbon to the benzene nucleus; the $CH\cdot NO_2$ group was originally united in one case to a phenyl and a nitro-group, and in the other to a phenyl group and a cyanogen group (Abstr., 1910, i, 192, 194).

A similar rearrangement is now found to occur with ω-nitrodiphenylmethane. On addition of a dilute aqueous solution of the potassium derivative of ω-nitrodiphenylmethane (1 mol.) to a well-cooled dilute solution of benzenediazonium chloride (1 mol.) containing excess of sodium acetate, an amorphous, yellow precipitate immediately separates, which must be regarded as the azo-compound, $NO_2\cdot CPh_2\cdot N_2Ph$. But this is unstable and undergoes intramolecular transposition into benzophenone-*p*-nitrophenylhydrazone (compare Hyde, Abstr., 1899, i, 688). Such rearrangement favours the structure $:C:NO\cdot OH$ rather than $:C<\begin{smallmatrix}O\\ |\\ N\cdot OH\end{smallmatrix}$ for the aci-nitrohydrocarbons (compare Steinkopf and Jürgens, this vol., i, 152).

The tendency of the nitro-group to pass from the complex $:CH\cdot NO_2$ to the benzene nucleus is shown also by the grouping $\cdot NH\cdot NO_2$, for example, nitroanilide, $C_6H_5\cdot NH\cdot NO_2$ or $C_6H_5\cdot N:NO_2H$, readily giving *p*-nitroaniline; here, too, the nitro-group passes preferably to the para-position. T. H. P.

New Synthesis of Chrysene. RICHARD WEITZENBÖCK and HANS LIEB (*Monatsh.*, 1912, **33**, 549—565).—On condensation of sodium 1-naphthylacetate with *o*-nitrobenzaldehyde in presence of acetic anhydride, α-1-naphthyl-*o*-nitrocinnamic acid,

$$C_{10}H_7\cdot C(CO_2H):CH\cdot C_6H_4\cdot NO_2,$$

is obtained, which, when reduced, gives the corresponding amino-compound. When this is diazotised and the diazonium sulphate solu-

tion shaken with copper powder, a new six-carbon ring is formed, namely, chrysene-6-carboxylic acid. On distillation, carbon dioxide is eliminated and chrysene obtained.

From 2-naphthylacetic acid by a similar series of reactions a hydrocarbon, m. p. 158—160°, in all probability 3 : 4-benzphenanthrene, has been obtained. All five isomeric hydrocarbons, $C_{18}H_{12}$, composed of four benzene rings with not more than two carbon atoms in common, are now known.

α-1-*Naphthyl*-o-*nitrocinnamic acid* crystallises in yellow needles or granules, m. p. 173—174°.

α-1-*Naphthyl*-o-*aminocinnamic acid* forms almost colourless needles, m. p. 175—176°.

Chrysene-6-*carboxylic acid* separates in almost colourless needles, m. p. 222—223°.

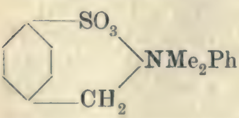
α-2-*Naphthyl*-o-*nitrocinnamic acid* crystallises in yellow needles, m. p. 177—178°.

α-2-*Naphthyl*-o-*aminocinnamic acid* also forms yellow needles, m. p. 191—192°

3 : 4-*Benzphenanthrene*-1-*carboxylic acid*, purified by sublimation in a vacuum, crystallises in needles, m. p. 243°. When sublimed at the ordinary pressure, the hydrocarbon, m. p. 158—160°, is obtained; it forms colourless platelets after crystallisation from alcohol.

E. F. A.

Preparation of Phenylbenzyldimethylammoniumsulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 245535).—*Phenylbenzyldimethylammoniumsulphonate* (annexed formula) is obtained by the methylation of calcium benzylmethylanilinesulphonate by the methods previously described for the corresponding disulphonic acid (Abstr., 1911, i, 852).



F. M. G. M.

Some Physical Constants of *cyclo*Hexanol. ROBERT DE FORCRAND (*Compt. rend.*, 1912, **154**, 1327—1330).—The considerable variation in the m. p. ascribed to *cyclo*hexanol is attributed to the facility with which this substance absorbs moisture. Dry *cyclo*hexanol has b. p. 160·9° (corr.)/766 mm., m. p. 22·45°, $D_4^{22.5}$ 0·9471. It crystallises in well-defined, quadratic octahedra. At 11°, 100 parts of *cyclo*hexanol dissolve 11·27 parts of water, whilst 100 parts of water dissolve 5·67 parts of *cyclo*hexanol.

H. W.

New Colouring Matters Derived from *p*-Aminodiphenyl Ether. ALPHONSE MAILHE (*Compt. rend.*, 1912, **154**, 1240—1242).—The dyes obtained by diazotising the *p*-aminodiphenyl ether described already (this vol., i, 346) and treating the product with various amines, phenols, etc., are described.

p-Aminodiphenyl ether yields a *hydrochloride*,

$$C_6H_5{\cdot}O{\cdot}C_6H_4{\cdot}NH_2,HCl,$$

m. p. 222°, and an *acetyl* derivative, m. p. 99°, crystallising in pearly leaflets. The diazotised product yields the following derivatives: with

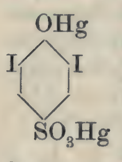
aniline, it gives the *azo*-compound, $C_6H_5 \cdot O \cdot C_6H_4 \cdot N\colon N \cdot C_6H_4 \cdot NH_2$, m. p. 88°, crystallising from alcohol in colourless needles, and giving red salts with acids. Diphenylamine gives the *azo*-derivative

$$C_6H_5 \cdot O \cdot C_6H_4 \cdot N\colon N \cdot C_6H_4 \cdot NHPh,$$

m. p. 38°, crystallising in yellow leaflets and giving in alcohol an intensely bluish-violet solution with acids, which turns green with excess of acid, and then deposits *green crystals*, m. p. 78°. With dimethylaniline, the *product* obtained crystallises in green lamellæ, m. p. 68°, and forms a carmine-red solution with hydrochloric acid, a yellow solution with sulphuric acid, and dyes silk or wool a golden-yellow in acid solution. α- and β-Naphthylamines yield a reddish-black *powder*, m. p. 75°, and a red *powder*, m. p. 115°, which in alcoholic solution are coloured violet and carmine-red respectively by sulphuric acid. With phenol the *compound*, $C_6H_5 \cdot O \cdot C_6H_4 \cdot N\colon N \cdot C_6H_4 \cdot OH$, m. p. 118°, yellow lamellæ, is formed; this gives a brown *monosulphonate*, which dyes silk or wool a dull brown. Resorcinol gives a *product*, m. p. 75°, crystallising in red needles. β-Naphthol yields a *substance* crystallising in yellow spangles. The naphtholsulphonic acids give *red dyes*, which dye cotton or wool directly carmine-red in acid baths.

In general, the azo-dyes derived from *p*-aminodiphenyl ether (phenoxyaniline) have a brighter tint than the corresponding aniline products, and melt at somewhat lower temperatures. T. A. H.

Preparation of a Mercurous Salt of Di-iodophenol-*p*-sulphonic Acid. H. TROMMSDORFF (D.R.-P. 245534).—*Mercurous di-iodophenol*-p-*sulphonate* (annexed formula) is obtained as a microcrystalline powder when mercurous nitrate (524 parts) dissolved in cold nitric acid is treated with sodium di-iodophenol-*p*-sulphonate (484 parts); it has a neutral reaction, and differs in mercury content, therapeutic action, and in other respects from the previously prepared mercuric di-iodophenol-*p*-sulphonate. The temperature must not rise above 30° during the reaction. F. M. G. M.



Separation of *m*- and *p*-Cresols. F. HOFFMANN–LA ROCHE & Co. (D.R.-P. 245892).—Numerous methods for separating *p*- and *m*-cresols have previously been advocated. It is now found that if the crude sulphonated mixture (after suitable dilution) is extracted with benzene at about 50°, a separation is effected; the unsulphonated *p*-cresol is recovered from the benzene by evaporation, whilst any unsulphonated *m*-cresol is separated from the crystallised *m*-cresolsulphonic acid by treatment with steam. F. M. G. M.

4-Amino-*o*-tolyl Mercaptan. THEODOR ZINCKE and HEINRICH ROLLHAÜSER (*Ber.*, 1912, 45, 1495—1511).—The preparation and reactions of 4-amino-*o*-tolyl mercaptan have been investigated.

Acetyl-p-*toluidine*-2-*sulphonic acid*, $NHAc \cdot C_6H_3Me \cdot SO_3H, H_2O$, was prepared by the sulphonation of aceto-*p*-toluidide with fuming sulphuric acid. Its *potassium* salt, $NHAc \cdot C_6H_3Me \cdot SO_3K, H_2O$, was analysed. The latter, after being dehydrated, was transformed by means of

phosphorus pentachloride into *acetyl*-p-*toluidine-2-sulphonyl chloride*, m. p. 124°, from which the corresponding *anilide*, m. p. 220—221°, was obtained. By reduction with zinc dust, the chloride was converted into 4-*acetylamino*-o-*tolyl mercaptan*, m. p. 95°. The acetyl group was eliminated from the latter by means of boiling hydrochloric acid, whereby the *hydrochloride* of 4-amino-*o*-tolyl mercaptan was obtained, which, when treated with sodium sulphide, yielded the free *base*, m. p. 47° (Hess, Abstr., 1881, 596, gives m. p. 42°), the *sulphate* and *diacetyl* derivative, m. p. 125°, of which were also examined.

4-Acetylamino-*o*-tolyl mercaptan was oxidised by ferric chloride to 4 : 4′-*diacetylaminoditolyl* 2 : 2′-*disulphide*, m. p. 220—221°, which, when boiled with aqueous-alcoholic hydrochloric acid, yielded the *hydrochloride* of 4 : 4′-diaminoditolyl 2 : 2′-disulphide, from which the free *base*, m. p. 94°, was liberated by means of ammonia.

4-Acetylamino-*o*-tolyl mercaptan was converted by methyl sulphate into 4-*acetylamino-2-methylthioltoluene*, m. p. 125—126°. The acetyl group was removed by hydrochloric acid, whereby 4-*amino-2-methylthioltoluene*, m. p. 47°, was obtained, the *hydrochloride* and *sulphate* of which were examined.

By the action of methyl iodide, 4-amino-2-methylthioltoluene was transformed into 2-*methylthiol*-p-*tolyltrimethylammonium iodide*, m. p. 200—202° (decomp.), which combined with bromine to yield a *perbromide*, $C_{11}H_{18}NSIBr_2$, m. p. 132° (decomp.), and with iodine to yield two *periodides*, $C_{11}H_{18}NSI,I_2$ and $C_{11}H_{18}NSI,I_4$. When chlorinated in glacial acetic acid solution, it formed a *compound*, m. p. 168—170° (decomp.), the composition of which is approximately that required by the formula $C_{11}H_{18}NSI,Cl_4$; when boiled with water, this deposited yellow *needles*, m. p. 161° (decomp.), which corresponded approximately with the formula $C_{11}H_{18}NSI,Cl_2$. 2-*Methylthiol*-p-*tolyltrimethylammonium chloride*, m. p. 134—137° (decomp.), was obtained when an aqueous solution of the corresponding iodide was heated with silver chloride. When the iodide was heated above its m. p., it decomposed with the formation of 4-*dimethylamino-2-methylthioltoluene*, b. p. 159°/17 mm., the *hydrochloride* of which was also analysed.

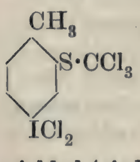
4-Amino-2-methylthioltoluene, when acted on by bromine in chloroform solution, yields a red bromine addition product, which, when dried and recrystallised from glacial acetic acid, was transformed into the *hydrobromide* of 5-bromo-4-amino-2-methylthioltoluene, from which the free *base*, m. p. 72—73°, was liberated by alkali. Its *acetyl* derivative, m. p. 122—123°, was prepared by the action of bromine in glacial acetic acid solution on 4-acetylamino-2-methylthioltoluene, and when hydrolysed by hydrochloric acid yielded the *hydrochloride* of the above bromo-compound.

4-Acetylamino-2-methylthioltoluene was converted by nitric acid (D 1·4) in glacial acetic acid solution into 5-*nitro-4-acetylamino-2-methylthioltoluene*, m. p. 163—164°, from which 5-*nitro-4-amino-2-methylthioltoluene*, m. p. 163°, was readily obtained. Stannous chloride reduced the latter to a *diamine*, which condensed with benzil to a *quinoxaline* derivative, m. p. 211—212°.

Hydrogen peroxide oxidised a solution of 4-acetylamino-2-methylthioltoluene in glacial acetic acid to *acetyl*-p-*toluidine*-2-*methylsulphoxide*, which separated from water $+1H_2O$, m. p. about 150°. The anhydrous substance has m. p. 150—151°. Potassium hydroxide transformed it into p-*toluidine*-2-*methylsulphoxide*, which crystallised from water $+1H_2O$, m. p. 90—95°, and from benzene in needles, m. p. 120—121°. Fuming hydrobromic acid converted each of the abovementioned substances into an unstable *perbromide*, which readily passed into the hydrobromide of 5-bromo-4-amino-2-methylthioltoluene.

Acetyl-p-*toluidine*-2-*methylsulphone*, m. p. 171°, was obtained by the oxidation of 4-acetylamino-2-methylthioltoluene by excess of hydrogen peroxide or potassium permanganate. Hydrochloric acid hydrolysed it to p-*toluidine*-2-*methylsulphone*, m. p. 91°. When the above oxidation was accomplished by means of potassium permanganate, 4-*acetylamino*-2-*methylsulphonebenzoic acid*, $C_{10}H_{11}O_5NS,H_2O$, m. p. 260—261°, was also formed. Oxidation of 4-amino-2-methylthioltoluene in glacial acetic acid solution by means of hydrogen peroxide yielded 2 : 2′-*methylsulphone*-4 : 4′-*azoxytoluene*, m. p. 213—215°.

4-Amino-2-methylthioltoluene was readily diazotised. Its *diazonium chloride* had m. p. 70—72° ; its *diazonium dichromate* was orange coloured. The former was readily transformed into 4-*cyano*-2-*methylthioltoluene*, m. p. 57—58°, which yielded the corresponding *acid*, m. p. 169°, on saponification. 4-*Iodo*-2-*methylthioltoluene*, b. p. 176°/16 mm., D 1·53, was obtained from the diazonium chloride and potassium iodide. When treated with bromine in chloroform solution it yielded hydrobromic acid, together with a *perbromide* crystallising in red needles, which, on exposure to moist air, was converted into a mixture of 5-*bromo*-4-*iodotolyl*-2-*methylsulphoxide*, m. p. 184°, and 5-*bromo*-4-*iodo*-2-*methylthioltoluene*, m. p. 72°. The latter was more readily prepared by the action of chloroform and bisulphite on the perbromide.



4-Iodo-2-methylthioltoluene, when dissolved in chloroform and treated with dry chlorine, yielded 2-*trichloromethylthioltolyl* 4-*iodochloride* (annexed formula), which, when shaken with chloroform and potassium iodide, yielded 4-*iodo*-2-*trichloromethylthioltoluene*, m. p. 44—45°. Aniline transformed the latter into triphenylguanidine and 4-*iodo*-o-*tolyl mercaptan*, m. p. 33—34°.

Syntheses in the Fatty Aromatic Series. IV. Mercaptans. JULIUS VON BRAUN (*Ber.*, 1912, 45, 1563--1567. Compare Abstr. 1911, i, 968)—Homologues of benzyl mercaptan were prepared in order to study the influence of the fatty-aromatic group on the odour of the compound ; the results prove that the sulphydryl group has by far the larger influence, even when the relatively small effect of the hydrocarbon residue, $C_6H_5{\cdot}CH_2$. is reinforced by increasing the number of methylene groups.

β-Phenylethyldithiourethane, $CH_2Ph{\cdot}CH_2{\cdot}S{\cdot}CS{\cdot}NH_2$, prepared by interaction of β-phenylethyl bromide with ammonium dithiocarbamate, crystallises in large, odourless platelets with silvery lustre, m. p. 66°. On heating under reduced pressure, *β-phenylethyl mercaptan* is formed.

This is better prepared by warming the dithiourethane with sodium hydroxide. It forms a colourless liquid, b. p. 105°/23 mm., with a more disagreeable odour than benzyl mercaptan. The benzoyl derivative and disulphide are both oily.

γ-Phenylpropyldithiourethane, $CH_2Ph·CH_2·CH_2·S·CS·NH_2$, crystallises in colourless, odourless platelets, m. p. 71°.

γ-Phenylpropyl mercaptan is a transparent liquid, b. p. 109°/10 mm., very similar to the lower homologue.

ε-Phenylamyldithiourethane forms a colourless, solid mass, m. p. 75°.

ε-Phenylamyl mercaptan has b. p. 132—134°/10 mm. The odour is exceptionally disagreeable. E. F. A.

Preparation of Acylarylaminonaphtholsulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 245608).—6-*Formylanilino*-1-*naphthol*-3-*sulphonic acid* is readily prepared by the action of formic acid on 6-anilino-1-naphthol-3-sulphonic acid; it is isolated as a greyish-white mass; the *sodium* salt can be crystallised from dilute alcohol.

7-*Formylanilino*-1-*naphthol*-3-*sulphonic acid* is prepared in a similar manner from the isomeric aminonaphthol acid as a grey, resinous mass; these compounds combine readily with diazonium salts, but do not react with nitrous acid. F. M. G. M.

Some *cyclo*Pentane Glycols. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1912, **154**, 1625—1627. Compare Abstr., 1911, i, 385; this vol., i, 34).—*cyclo*Pentan-1:2-diol, already obtained by Meiser (Abstr., 1899, i, 741), can be obtained by converting the dibromide into the diacetate and hydrolysing this by alcoholic potash. It can also be obtained from the iodohydrin, which is prepared by the action of iodine and mercuric oxide on *cyclo*pentene, by hydrolysis in the cold with potassium hydroxide, which produces the internal ether; this can be hydrated to the alcohol by heating with water for several hours at 125°. The latter method of preparation indicates a *cis*-configuration.

The *trans*-stereoisomeride can be obtained by the oxidation of *cyclo*pentene with potassium permanganate; it has b. p. 130°/20 mm., m. p. 10°; *diphenylurethane*, m. p. 195°.

The dehydration of *cyclo*pentanyl*cyclo*pentanol, $C_5H_9·C_5H_8·OH$ (Godchot and Taboury, Abstr., 1911, i, 385), by distillation with zinc chloride yields a cyclo*pentanyl*cyclo*pentene*, b. p. 190°, D^{18} 0·9183, n^{18} 1·4953. Treatment with bromine in the presence of aluminium bromide converts this substance into a *derivative*, $C_{10}H_4Br_6$, m. p. 308—309°. The hydrocarbon with bromine in carbon disulphide solution gives the *dibromide*, m. p. 160°, which can be hydrolysed by potassium carbonate to cyclo*pentanyl*cyclo*pentan*-1:2-*diol*, b. p. 189—190°, m. p. 87—88°. As this is also obtainable from the *cyclo*pentanyl*cyclo*pentene by the action of iodine and mercuric oxide with subsequent hydrolysis of the resultant iodohydrin by potassium carbonate, it is probably of *cis*-configuration. D. F. T.

Nitro-derivatives of Diphenylene Oxide. ALPHONSE MAILHE (*Compt. rend.*, 1912, **154**, 1515—1517).—Diphenylene oxide is attacked by fuming nitric acid, giving a viscous, brown mass; this on treatment with ether goes to a yellow powder, which by treatment with benzene and then with alcohol can be separated into three nitro-compounds: *Dinitrodiphenylene oxide*, $O<\begin{matrix}C_6H_3\cdot NO_2\\ | \\ C_6H_3\cdot NO_2\end{matrix}$, m. p. 245°, in which the nitro-groups are probably *para* to the oxygen, *tetranitrodiphenylene oxide*, $O<\begin{matrix}C_6H_2(NO_2)_2\\ | \\ C_6H_2(NO_2)_2\end{matrix}$, m. p. 168°, and *pentanitrodiphenylene oxide*, $O<\begin{matrix}C_6H(NO_2)_3\\ | \\ C_6H_2(NO_2)_2\end{matrix}$, m. p. 122°, the first being the principal product. The dinitro-derivative on reduction with iron and acetic acid yields a *diamine*, m. p. 125°, which gives a red coloration with ferric chloride.

Further nitration of the polynitro-derivatives by means of a mixture of sulphuric and fuming nitric acids gives *hexanitrodiphenylene oxide*, $O<\begin{matrix}C_6H(NO_2)_3\\ | \\ C_6H(NO_2)_3\end{matrix}$, m. p. 135°. No higher nitro-compound could be obtained, but the hexanitro-compound on warming with fuming sulphuric acid yields *hexanitrodisulphodiphenylene oxide*,

$$O<\begin{matrix}C_6(NO_2)_3\cdot SO_3H\\ | \\ C_6(NO_2)_3\cdot SO_3H\end{matrix},$$

a white powder, m. p. 215°.

Nitration of diphenylene oxide in acetic acid solution yields the mononitro-derivative already described by Borsche and Bothe (Abstr., 1908, i, 528). W. G.

Preparation of Homopiperonylamine. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 245523. Compare Abstr., 1908, i, 901; 1911, i, 483).—Homopiperonylamine (Abstr., 1906, i, 421), finds employment in the preparation of hydrastinine; it is now found that it can be readily prepared by the reduction of homopiperonal oxime with sodium amalgam in a mixture of equal parts of alcohol and acetic acid, and that the foregoing oxime can be obtained by the reduction of methylenedioxy-ω-nitrostyrene (obtained by the action of nitromethane on piperonal) with zinc dust in alcoholic acetic acid solution. F. M. G. M.

Action of Sodium Methoxide on Trinitroveratrole. JAN J. BLANKSMA (*Chem. Weekblad*, 1912, **9**, 440—441).—The constitution of the compound with m. p. 152° obtained from trinitroveratrole by the action of sodium methoxide (Abstr., 1905, i, 277) is proved to be 5 : 6-*dinitro*-1 : 2 : 4-*trimethoxybenzene*. There is simultaneously formed the isomeride with m. p. 92°, 3 : 5-dinitro-1 : 2 : 4-trimethoxybenzene, the proportion of the first isomeride to the second being as 3 : 1.

The diethyl ether of 3 : 4 : 5-trinitrocatechol is converted by sodium ethoxide into 5 : 6-*dinitro*-1 : 2 : 4-*triethoxybenzene*, m. p. 133°.

A. J. W.

Optically Active Phenylmethylcarbinols. ROBERT H. PICKARD and JOSEPH KENYON (*Ber.*, 1912, **45**, 1592—1593. Compare Holmberg, this vol., i, 448).—The value for the optical rotatory power of *d*-phenylmethylcarbinol given by Holmberg indicates that much racemisation had occurred in his material (compare Pickard, Trans., 1911, **99**, 45).

The two secondary octyl alcohols, $[\alpha]_D^{20} \pm 9\cdot9°$, are converted quantitatively into the corresponding bromo-compounds, $[\alpha]_D^{20} \pm 27\cdot5°$, from which by means of moist silver oxide the alcohols can be recovered. Some octylene is also formed. E. F. A.

Search for Cholesterol in Java Petroleum. WILHELM STEINKOPF, A. K. KOSS, and S. LIEBMANN (*Chem. Zeit.*, 1912, **36**, 653—654. Compare Molinari and Fenaroli, Abstr., 1908, i, 933, and Koss, Abstr., 1911, i, 761).—Application of Windaus' digitonin test for cholesterol to the lævorotatory fractions of Java petroleum show that these do not contain cholesterol. It is further shown that on distilling petroleum containing cholesterol, the latter does not pass over in the lower fractions, so that if it occurs in petroleum it will probably be found in the portions boiling at about 300° under reduced pressure. These results show that the lævorotation of the lower boiling fractions of Java petroleum cannot be due to the presence of unchanged cholesterol, although it may be due to its decomposition.

T. A. H.

New Halogen Derivatives of Cholesterol. RICHARD KOLM (*Monatsh.*, 1912, **33**, 447—450).—*Cholesteryl bromide*, prepared by the action of phosphorus tribromide on cholesterol in benzene solution, crystallises in nacreous platelets, m. p. 98°. A particularly fine play of colour is obtained on melting it and allowing it to cool again. It has $[\alpha]_D^{19\cdot5} - 19\cdot14°$.

It reacts with bromine in acetic acid to form *tribromocholestan*, $C_{27}H_{43}Br_3$, which crystallises in well-formed, short prisms, m. p. 111—112°, $[\alpha]_D^{19} - 49\cdot82°$ without mutarotation.

Cholesteryl iodide has also been obtained. E. F. A.

Preparation of Glycol Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 245532).—When halogenated glycols are heated with benzoic or substituted benzoic acids (with the exception of salicylic acid), esterification readily occurs; the following compounds have been prepared.

Ethylene o-*toluate*, b. p. 158°/10 mm.; *ethylene benzoate*, b. p. 176—180°/20 mm., m. p. 45°, is prepared by heating sodium benzoate and ethylene glycol chlorohydrin together during three to four hours at 145, or by heating β-chloroethyl benzoate during one or two hours with a concentrated solution of sodium acetate at 130°.

Ethylene o-*chlorobenzoate*, b. p. 205°/20 mm., is obtained in a similar manner from ethylene dichloride and sodium *o*-chlorobenzoate, and *ethylene* p-*nitrobenzoate*, m. p. 63°, from *p*-nitrobenzoic acid and glycol in the presence of sulphuric acid. F. M. G. M.

Condensation of Alkyl-*o*-toluidines with Carbonyl Chloride. BERTHOLD RASSOW and OTTO REUTER (*J. pr. Chem.*, 1912, [ii], 85, 489—497).—A record of unsuccessful attempts to prepare tetramethyldiaminodi-*o*-tolyl ketone by the interaction of carbonyl chloride and dimethyl-*o*-toluidine. When heated at 160° in the presence of aluminium chloride, these substances react, yielding (1) methyl chloride; (2) s-*di-o-tolyldimethylcarbamide*, $CO(NMe{\cdot}C_7H_7)_2$, which crystallises in lustrous, silvery leaflets, m. p. 90°, and yields a *tetranitro*-derivative as a yellow powder sintering at 80° (decomp. 110—115°); (3) *dimethylamino-o-toluo-N-methyl-o-toluidide*, $NMe_2{\cdot}C_6H_4Me{\cdot}CO{\cdot}NMe{\cdot}C_6H_4Me$, which forms rhombic platelets, and yields a *picrate*,

$$C_{18}H_{22}ON_2,C_6H_3O_7N_3,$$

crystallising in needles, m. p. 158°.

s-*Di-o-tolyldiethylcarbamide*, $CO(NEt{\cdot}C_7H_7)_2$, prepared by heating *N*-ethyl-*o*-toluidine with carbonyl chloride in the presence of aluminium chloride, has m. p. 37—39°, b. p. 188°/12 mm. F. B.

$\alpha\alpha'$-Ethylenebisimino-acids. N. SCHLESINGER (*Ber.*, 1912, 45, 1486—1493. Compare Abstr., 1911, i, 427).—*$\alpha\alpha'$-Ethylenebisiminophenylacetonitrile*, $C_2H_4(NH{\cdot}CHPh{\cdot}CN)_2$, m. p. 122—123°, is prepared by the addition of benzaldehyde to a methyl alcoholic-aqueous solution of potassium cyanide and ethylenediamine hydrochloride. Its *hydrochloride* decomposes at about 148—154°. Boiling dilute mineral acids transform the nitrile into benzaldehyde, hydrogen cyanide, and ethylenediamine. Hydrolysis to the corresponding *acid* can be effected, however, by treatment of the nitrile with a mixture of concentrated sulphuric acid and fuming hydrochloric acid at the ordinary temperature and subsequent boiling of the diluted solution. It undergoes no apparent change when heated to 250°. Its *hydrochloride* is very sparingly soluble in water. Its *copper* salt, $C_{18}H_{18}O_4N_2Cu$, was analysed. Its *methyl* ester, prepared by the Fischer-Speier method, forms a viscous, yellow liquid, which decomposes when heated, even under diminished pressure, and has D_4^{20} 1·1501, n_D^{20} 1·5448. The similar *ethyl* ester has D_4^{20} 1·1091, n_D^{20} 1·5320, and forms a crystalline *hydrochloride* when its ethereal solution is treated with dry hydrogen chloride.

$\alpha\alpha'$-Ethylenebisiminopropionitrile hydrochloride, $C_8H_{14}N_4,2HCl$, is obtained when dry hydrogen chloride is passed into a dry ethereal solution of the product of the reaction of ethylenediamine hydrochloride, acetaldehyde, and potassium cyanide. Aqueous acids hydrolyse it completely. A mixture of concentrated sulphuric acid and fuming hydrochloric acid converts it into the corresponding *acid*, m. p. about 262° (decomp.), from which the *hydrochloride*, m. p. about 214° (decomp.), *copper* salt, $C_8H_{14}O_4N_2Cu$, and *ethyl* ester were prepared. The latter has b. p. 170°/14 mm., D_4^{20} 1·0297, n_D^{20} 1·4483, and appears to be slightly impure.

In a similar manner, $\alpha\alpha'$-ethylenebisimino-α-phenylpropionitrile, $C_2H_4(NH{\cdot}CMePh{\cdot}CN)_2$, m. p. 108—109° (decomp.), is formed by the reaction of ethylenediamine hydrochloride, potassium cyanide, and acetophenone. A mixture of concentrated sulphuric and fuming hydrochloric acids transforms it into the corresponding *acid*, the *hydro-*

chloride and *copper* salt of which are also described. This acid cannot apparently be esterified by the Fischer-Speier method.

aa'-Ethylenebisiminodiphenylacetonitrile, $C_2H_4(NH\cdot CPh_2\cdot CN)_2$, is slowly formed in poor yield when ethylenediamine hydrochloride, benzophenone, and potassium cyanide react at the ordinary temperature in aqueous-methyl alcoholic solution. It melts indefinitely at 158—163° (decomp.). Its hydrolysis has not been effected. H. W.

Diphenyl*iso*propylacetic [*aa*-Diphenyl-*β*-methylbutyric] Acid. (Mme.) PAULINE RAMART-LUCAS (*Compt. rend.*, 1912, **154**, 1617—1620).—The acid obtained earlier (Ramart-Lucas, this vol., i, 449) is monobasic, giving a silver salt, $C_{17}H_{17}O_2Ag$, and on treatment with thionyl chloride gives an *acid chloride*, $C_{17}H_{17}OCl$, m. p. 95—96°; this is converted by ammonia into the *amide*, needles, m. p. 149°. It is therefore possibly a diphenyldimethylpropionic acid or *aa*-diphenyl-*β*-methylbutyric acid; the properties do not agree with those of the *ββ*-diphenyl-*aa*-dimethylpropionic acid already described by Nef (Abstr., 1902, i, 8), and so attempts were made to synthesise *aa*-diphenyl-*β*-methylbutyric acid for the purpose of comparison.

The condensation of dimethylpyruvic acid with benzene gives an acid, m. p. 150—151°, which proves to be identical with the dimethylatropic acid, $CMe_2:CPh\cdot CO_2H$, of Blaise and Courtot (Abstr., 1906, i, 794); it is evidently produced here by the elimination of a molecule of water from the primarily formed *a-iso*propylmandelic acid.

By the action of diphenylacetyl chloride on excess of benzene in the cold, the main product obtained is triphenylvinyl alcohol, $CPh_2:CPh\cdot OH$ (compare Biltz, Abstr., 1893, i, 718), but in the warm the product is the ketonic isomeride diphenylacetophenone, $CHPh_2\cdot COPh$ (oxime, m. p. 180°; compare Kohler, Abstr., 1906, i, 756). All endeavours to introduce the *iso*propyl group into either of these substances were unsuccessful, the sodium amide causing scission into diphenylmethane and benzamide.

By treating diphenylacetonitrile with sodium amide and *iso*propyl iodide in benzene, *aa-diphenyl-β-methylbutyronitrile* is obtained as a viscous liquid, b. p. 193—195°/15 mm., which can be hydrolysed by a mixture of hydrochloric and acetic acids to *aa-diphenyl-β-methylbutyric acid*, m. p. 163°, and the *anhydride*, m. p. 166°; a neutral *substance*, $C_{16}H_{16}O_2$, m. p. 109—110°, is obtained as a by-product. The acid is not identical with the acid the constitution of which is under investigation. D. F. T.

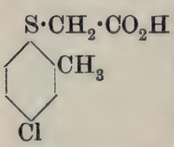
Preparation of Acetonechloroform Acetylsalicylate [*o*-Acetoxybenzoate]. RICHARD WOLFFENSTEIN (D.R.-P. 245533).—*Acetonechloroform* o-*acetoxybenzoate*, fine needles, m. p. 54—57° (sintering about 49°), b. p. about 185°/ in a vacuum, with partial decomposition, is readily prepared by heating acetonechloroform with *o*-acetoxybenzoyl chloride in the presence of a tertiary base, such as quinoline; it is of therapeutic value. F. M. G. M.

Preparation of Menthyl Acetylsalicylate [*o*-Acetoxybenzoate]. KONTOR CHEMISCHER PRÄPARATE ERNST ALEXANDER (D.R.-P. 244787).—*Menthyl* o-*acetoxybenzoate*, an odourless, tasteless liquid,

D^{15} 1·0635, b. p. 212—215°/14 mm., is obtained by treating menthyl salicylate (prepared from menthol and salicylic acid) with the ordinary acetylating agents. The following yields are obtainable: with acetyl chloride in xylene, 75%; acetic acid with sulphuric acid, 60%, and with acetic anhydride, 90—95%. F. M. G. M.

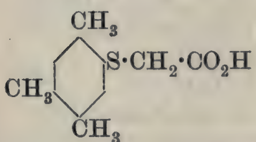
[Preparation of 3 : 4-Dichlorophenylthiolacetic Acid.] KALLE & Co. (D.R.-P. 245633).—3 : 4-*Dichlorophenylthiolacetic acid*, colourless needles, is prepared from 3 : 4-dichloroaniline by methods described previously; when treated with fuming sulphuric acid, it furnishes a dye in the form of a violet powder. F. M. G. M.

Preparation of 4-Chloro-*o*-tolylthiolacetic Acid. KALLE & Co. (D.R.-P. 245631. Compare this vol., i, 354).—4-*Chloro-*o*-tolylthiolacetic acid* (annexed formula), colourless needles, is prepared from *p*-chloro-*o*-toluidine; the dye it furnishes with sulphuric acid is a bluish-red powder and suitable for wool or cotton. F. M. G. M.



[Preparation of 4-Chloro-*m*-tolylthiolacetic Acid.] KALLE & Co. (D.R.-P. 245632).—4-*Chloro-*m*-tolylthiolacetic acid*, colourless needles, is prepared from *p*-chloro-*m*-toluidine; when treated with fuming sulphuric acid it furnishes a reddish-violet powder, the tinctorial properties of which are described in the original. F. M. G. M.

[Preparation of ψ-Cumylthiolacetic Acid.] KALLE & Co. (D.R.-P. 245630. Compare this vol., i, 354). —*ψ-Cumylthiolacetic acid* (annexed formula), colourless needles, is prepared by previously described methods from ψ-cumidine; the dye formed by treating it with concentrated or fuming sulphuric acid is a dark violet powder, which dyes cotton a bluish-violet shade, and wool a violet-red tone. F. M. G. M.



Derivatives of Benzilic Acid and of Chlorodiphenylacetic Acid. HEINRICH KLINGER (*Annalen*, 1912, **389**, 253—264).—*a-Chlorodiphenylacetanilide*, $CPh_2Cl·CO·NHPh$, m. p. 88°, is prepared from aniline and chlorodiphenylacetyl chloride in ether. Its chlorine is very reactive, and is easily substituted by boiling methyl or ethyl alcohol, yielding *a-methoxydiphenylacetanilide*,

$$OMe·CPh_2·CO·NHPh,$$

m. p. 149—150°, rhombic crystals [$a : b : c = 0·64344 : 1 : 0·48788$], or *a-ethoxydiphenylacetanilide*, m. p. 130—131°. *a-Anilinodiphenylacetanilide*, $NHPh·CPh_2·CO·NHPh$, m. p. 181—182°, obtained by warming chlorodiphenylacetanilide and aniline (4 mols.) on the water-bath, yields by hydrolysis *benzilanilide*, $OH·CPh_2·CO·NHPh$, m. p. 175°, monoclinic crystals [$a : b : c = 0·97296 : 1 : 0·89641 ; \beta = 86°16'47''$].

a-p-Toluidinodiphenylaceto-p-toluidide, $C_7H_7·NH·CPh_2·CO·NH·C_7H_7$, m. p. 168°, obtained from a-chlorodiphenylacetyl chloride and *p*-toluidine at 125—130°, is converted into *benzilo-p-toluidide*,

$$OH·CPh_2·CO·NH·C_7H_7,$$

m. p. 189—190°, by boiling concentrated hydrochloric acid. When gently warmed and finally heated at 150°, α-chlorodiphenylacetyl chloride and methylaniline (4 mols.) yield *α-methylanilinodiphenylaceto-methylanilide*, $NMePh\cdot CPh_2\cdot CO\cdot NMePh$, m. p. 212°.

Ethyl α-chlorodiphenylacetate and *methyl α-chlorodiphenylacetate* (impure), obtained by passing hydrogen chloride into an ethyl or methyl-alcoholic solution of benzilic acid, yield with *p*-toluidine on the water-bath *ethyl α-p-toluidinodiphenylacetate*, $C_7H_7\cdot NH\cdot CPh_2\cdot CO_2Et$, m. p. 137°, monoclinic crystals [$a:b:c = 1\cdot4383:1:0\cdot9503$; $\beta = 48°25'58''$], or the *methyl* ester, m. p. 134—135°. *α-p-Toluidinodiphenylacetic acid*, obtained by the hydrolysis of the preceding esters, has decomp. 150°. C. S.

Diphenyleneglycollic, α-Chlorodiphenyleneacetic, and α-Bromodiphenyleneacetic Acids. HEINRICH KLINGER (*Annalen*, 1912, **389**, 237—253)—Diphenyleneglycollic acid is obtained in 94% yield by heating phenanthraquinone with 10 parts of 20% sodium hydroxide for two and a-half to three hours at 70—80° in a current of air. It has m. p. 166—167°, and forms a *methyl* ester, m. p. 159°. This ester or the ethyl ester is obtained by passing a little hydrogen chloride into a dilute methyl or ethyl alcoholic solution (1 : 25) of the acid; with more concentrated solutions, at higher temperatures, and with an increased quantity of hydrogen chloride, the alcoholic hydroxyl group of the acid is replaced by chlorine; thus a solution of the acid in methyl alcohol (1 : 5), saturated at 0° with hydrogen chloride and then heated at 100° for six hours, yields *methyl α-chlorodiphenyleneacetate* [*9-chlorofluorene-9-carboxylate*], $\begin{array}{l}C_6H_4\\|\\C_6H_4\end{array}\!\!>CCl\cdot CO_2Me$, m. p. 113°, which is also prepared by the action of chlorodiphenyleneacetyl chloride on cold methyl alcohol. *Chlorodiphenyleneacetamide*, obtained from the chloride and cold ethereal ammonia, has m. p. 194°. Chlorodiphenyleneacetyl chloride and aniline (2 mols.) in ether yield chlorodiphenyleneacetanilide, which is converted into *α-ethoxydiphenyleneacetanilide*, $\begin{array}{l}C_6H_4\\|\\C_6H_4\end{array}\!\!>C(OEt)\cdot CO\cdot NHPh$, m. p. 129°, by prolonged boiling with alcohol. The chloride and aniline (4 mols.) in ether yield *α-anilinodiphenyleneacetanilide*, $\begin{array}{l}C_6H_4\\|\\C_6H_4\end{array}\!\!>C(NHPh)\cdot CO\cdot NHPh$, m. p. 199—200°, which is scarcely attacked by boiling concentrated hydrochloric acid, but is converted into *diphenyleneglycollanilide*, m. p. 247°, by hydrochloric acid at 110—120°

α-Bromodiphenyleneacetyl bromide, $\begin{array}{l}C_6H_4\\|\\C_6H_4\end{array}\!\!>CBr\cdot COBr$, m. p. 137—138°, yellow prisms, obtained from diphenyleneglycollic acid and phosphorus pentabromide, is converted into *methyl α-bromodiphenyleneacetate*, m. p. 108·5—109°, or the *ethyl* ester, m. p. 76°, by cold methyl or ethyl alcohol, into *α-bromodiphenyleneacetamide*, m. p. 175°, by ammonia in benzene, and into *α-bromodiphenyleneacetanilide*, m. p. 166°, by aniline in cold benzene. C. S.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. VI. Partial Methylation of Phenolcarboxylic Acids. EMIL FISCHER and OTTO PFEFFER (*Annalen*, 1912, 389, 198—214. Compare Abstr., 1911, i, 874).—The ortho-methylated derivatives of gentisic, β-resorcylic, and phloroglucinolcarboxylic acids have been obtained by treating the methylcarbonato-derivatives with diazomethane and hydrolysing the products.

5-Methylcarbonato-2-hydroxybenzoic acid is converted by cold ethereal diazomethane by rapid treatment into *methyl 5-methylcarbonato-2-hydroxybenzoate*, $CO_2Me\cdot O\cdot C_6H_3(OH)\cdot CO_2Me$, colourless needles, m. p. 75—76° (corr.) (reddish-violet coloration with alcoholic ferric chloride), and by prolonged treatmeut (twenty hours at 25°) into *methyl 5-methylcarbonato-2-methoxybenzoate*, m. p. 92—93° (corr.). The latter does not develop a coloration with ferric chloride, and in alcoholic solution is converted by 2*N*-sodium hydroxide on the water-bath, and subsequent acidification, into 5-*hydroxy-2-methoxybenzoic acid*, m. p. 155—156° (corr.). In a similar manner, by prolonged treatment with ethereal diazomethane at 25°, 4-methylcarbonato-2-hydroxybenzoic acid yields *methyl 4-methylcarbonato-2-methoxybenzoate*, m. p. 64—65° (corr.), the hydrolysis of which by 2*N*-sodium hydroxide (4 mols.) at 25° for twenty-four hours and subsequent acidification followed by treatment of the product with 8% potassium hydrogen carbonate ields 4-*hydroxy-2-methoxybenzoic acid*, m. p. 185—187° (decomp. corr.). *Methyl 4-methylcarbonato-2 : 6-dimethoxybenzoate*, m. p. 105—106° (corr.), obtained from 4-methylcarbonato-2 : 6-dihydroxybenzoic acid and ethereal diazomethane, is hydrolysed by 2*N*-sodium hydroxide at 25°, yielding *methyl 4-hydroxy-2 : 6-dimethoxybenzoate*, m. p. 189° (corr.), which is then hydrolysed by concentrated sulphuric acid at 25° to 4-*hydroxy-2 : 6-dimethoxybenzoic acid*, decomp. 175° (corr.). By direct hydrolysis with cold concentrated sulphuric acid, methyl 4-methylcarbonato-2 : 6-dimethoxybenzoate yields 4-*methylcarbonato-2 : 6-dimethoxybenzoic acid*, m. p. 160° (corr.). It has been found that the methylcarbonato-derivatives of other phenolcarboxylic acids are stable to cold concentrated sulphuric acid.

Methyl 3 : 5-dimethylcarbonato-4-methoxybenzoate, m. p. 66—67°, obtained from 3 : 5-dimethylcarbonato-4-hydroxybenzoic acid and diazomethane, is hydrolysed by 2*N*-sodium hydroxide at 40° in an atmosphere of hydrogen, yielding after acidification 3 : 5-dihydroxy-4-methoxybenzoic acid. C. S.

Phthalyl Chloride. JOHANNES SCHEIBER (*Annalen*, 1912, 389, 121—168).—The asymmetric constitution, $C_6H_4<\substack{CCl_2\\CO}>O$, of phthalyl chloride is based on, amongst other evidence, its behaviour on reduction, its interaction with benzene to form phthalophenone in the Friedel-Crafts' reaction, the formation of diethylphthalide from the chloride and zinc ethyl, and its condensation with the sodium derivatives of substances containing the group ·CH:C(OH)·, such as ethyl malonate, ethyl acetoacetate, ethyl benzoylacetate, ethyl cyanoacetate, benzoyl-

acetone, and acetylacetone, to form compounds of the types:

$$CO<\substack{C_6H_4\\O}>C:C(CO_2Et)_2,$$

$CO<\substack{C_6H_4\\O}>C[CH(CO_2Et)_2]_2$ and $\begin{array}{l}C_6H_4\cdot C:C(CO_2Et)_2\\ CO-C(CO_2Et)_2\end{array}$ (taking ethyl malonate as an example).

The author is of opinion, however, that this evidence is by no means conclusive. The formation of phthalophenone from phthalyl chloride, benzene, and aluminium chloride is conditioned by the temperature, since in cold carbon disulphide the chief product of the reaction is benzoylbenzoic acid, the formation of which is evidence in favour of the symmetric constitution of phthalyl chloride. Again, the formation of the preceding three types of condensation products has been regarded as proving the asymmetric constitution of phthalyl chloride (compare Bülow, Abstr., 1905, i, 529). The constitutions of these products are deduced from their behaviour on hydrolysis, on reduction by zinc and acetic acid, and additive behaviour with sodium ethoxide. The author shows, however, that the properties and behaviour of the three types of condensation products are in better harmony with the formulæ: $C_6H_4<\substack{CO\\CO}>C(CO_2Et)_2$ $\left[\text{or } C_6H_4<\substack{CO-C\cdot CO_2Et\\CO\cdot O\cdot C\cdot OEt}\right]$,

$$C_6H_4<\substack{CO\cdot CH(CO_2Et)_2\\CO\cdot CH(CO_2Et)_2},$$

and $C_6H_4<\substack{C[:C(CO_2Et)_2]\\C[:C(CO_2Et)_2]}>O$, which represent the products as derivatives of a phthalyl chloride of symmetric structure. The only way in which products of the first type can be derived from a phthalyl chloride of asymmetric structure is for the initially formed phthalide derivatives to change to substituted indandiones by a process similar to that whereby benzylidenephthalide is converted into 2-phenylindandione. This rearrangement, however, requires the presence of alcohol (Eibner, Abstr., 1906, i, 588). The author shows that in ethereal solution benzylidenephthalide is unchanged by ethyl sodioacetoacetate, and acetonylenephthalide is not rearranged to 2-acetylindandione by sodioacetylacetone.

The proposed new formulæ of substances of the first-mentioned type explain the behaviour of these substances on hydrolysis, particularly the formation of phthalamide by hydrolysis with ammonia. With regard to the action of zinc and acetic acid, Wislicenus regards the change $CO<\substack{C_6H_4\\O}>C:C(CO_2Et)_2 \longrightarrow CO_2H\cdot C_6H_4\cdot CH_2\cdot CH(CO_2Et)_2$ as conclusive evidence of the constitution of ethyl phthalylmalonate. It is open to question, however, whether substances with such constitutions undergo reduction and fission as indicated; for example, benzylidenephthalide is unchanged by zinc and acetic acid. The author represents the reduction of ethyl phthalylmalonate by the scheme:

$C_6H_4<\substack{CO\\CO}>C(CO_2Et)_2 \longrightarrow CO_2H\cdot C_6H_4\cdot CH(OH)\cdot CH(CO_2Et)_2 \longrightarrow$ $CO_2H\cdot C_6H_4\cdot CH:C(CO_2Et)_2 \longrightarrow CO_2H\cdot C_6H_4\cdot CH_2\cdot CH(CO_2Et)_2$, and in favour of this view finds that ethyl benzoylmalonate is reduced, in

part, to ethyl benzylmalonate by zinc and boiling acetic acid. The constitution, $CO<\substack{C_6H_4 \\ -O-}>C:CAcBz$, of phthalylbenzoylacetone cannot be regarded as definitely proved by the reduction of the substance to phthalidylbenzoylacetone (Bülow and Koch, Abstr., 1904, i, 321), because the similarly constituted compounds, ethyl phthalylmalonate and ethyl phthalylacetoacetate, do not yield phthalidyl derivatives by reduction; the former yields a little ethyl *o*-carboxybenzylmalonate, whilst the latter is converted partly into an isomeride, m. p. 96—97° (see below), partly into ethyl *o*-carboxybenzylacetoacetate.

The fact that the additive compound of ethyl phthalylmalonate and sodium ethoxide yields by acidification a substance which develops an intense red coloration with ferric chloride, is in favour of the author's new constitution of ethyl phthalylmalonate, which permits of the production of an additive compound, $CO_2Et\cdot C_6H_4\cdot CO\cdot CH(CO_2Et)_2$ or $CO_2Et\cdot C_6H_4\cdot CO\cdot C(CO_2Et):C(OH)\cdot OEt$, containing, or giving by enolisation, a hydroxyl group. The properties of the additive compound of sodium ethoxide and ethyl phthalylacetoacetate are explained best by ascribing to the latter the constitution $C_6H_4<\substack{CO \\ CO}>CAc\cdot CO_2Et$, rather than $CO<\substack{C_6H_4 \\ -O-}>C:CAc\cdot CO_2Et$. Bülow's phenylhydrazone, m. p. 236°, of ethyl phthalylacetoacetate (Abstr., 1905, i, 529) is shown to be a pyrazole derivative. Also the so-called bishydrazones obtained by Bülow and Koch from phthalylbenzoylacetone and phenylhydrazine, *p*-nitrophenylhydrazine, and *p*-bromophenylhydrazine respectively in boiling acetic acid (*loc. cit.*) are proved to be anilinophthalimides, $C_6H_4<\substack{CO \\ CO}>N\cdot NHAr$, since the same substances are produced from phthalic anhydride and the corresponding hydrazine. The fission which phthalylbenzoylacetone must have undergone to yield these anilinophthalimides is also experienced by ethyl phthalylmalonate and by ethyl phthalylcyanoacetate under similar conditions. Both substances are converted into *phthalylbisphenylhydrazide*,

$$C_6H_4(CO\cdot NH\cdot NHPh)_2,$$

m. p. 161°, by phenylhydrazine; the former, however, in cold glacial acetic acid solution yields anilinophthalimide. *Phthalyldibenzoylmethane*, $C_{23}H_{14}O_4$, m. p. 162°, prepared from sodiodibenzoylmethane and phthalyl chloride in cold ether, reacts with phenylhydrazine in acetic acid or ether to form a *substance*, m. p. 234—236°, yellowish-red crystals, which receives the constitution

$$CO_2H\cdot C_6H_4\cdot CO\cdot CHBz\cdot CPh:N\cdot NHPh,$$

because it is soluble in sodium carbonate and develops a red coloration with ferric chloride, but does not respond to Bülow's reaction.

Ethyl phthalylmalonate and ethyl phthalylacetoacetate do not react additively with bromine or with ethyl diazoacetate. Ethyl α-cyanocinnamate and ethyl diazoacetate react at 100° to form nitrogen and *ethyl α-cyano-γ-phenyl*cyclo*propan-αβ-dicarboxylate*, a viscous oil.

By treatment with boiling glacial acetic acid for two hours, ethyl phthalylacetoacetate, m. p. 124°, is converted into an *isomeride*, m. p. 96—97°, colourless needles, which is reconverted into the original sub-

stance by a suspension of ethyl sodioacetoacetate in boiling ether. Both isomerides yield the same pyrazole and behave alike towards sodium ethoxide and towards zinc and acetic acid. The constitutions $C_6H_4{<}\substack{CO\\CO}{>}CAc\cdot CO_2Et$ and $C_6H_4{<}\begin{matrix}CO—C\cdot CO_2Et\\ CO\cdot O\cdot CMe\end{matrix}$ are proposed for the esters, m. p. 124° and 96—97° respectively. In a similar manner, phthalylbenzoylacetone, m. p. 175°, $C_6H_4{<}\substack{CO\\CO}{>}CAcBz$, is converted into an *isomeride*, m. p. 102°, $C_6H_4{<}\begin{matrix}CO—CBz\\ CO\cdot O\cdot CMe\end{matrix}$. The two known forms of ethyl phthalylcyanoacetate, m. p. 190—192° and 140—141° respectively, are represented by the formulæ $C_6H_4{<}\substack{CO\\CO}{>}C(CN)\cdot CO_2Et$ and $C_6H_4{<}\begin{matrix}CO—C\cdot CN\\ CO\cdot O\cdot C\cdot OEt\end{matrix}$. Ethyl phthalylmalonate, phthalylacetylacetone, and phthalyldibenzoylmethane have been obtained only in one form; the first and the last are respectively represented by the formulæ $C_6H_4{<}\substack{CO\\CO}{>}C(CO_2Et)_2$ and $C_6H_4{<}\substack{CO\\CO}{>}CBz_2$, whilst phthalylacetylacetone is probably the OC-derivative,

$$C_6H_4{<}\begin{matrix}CO—CAc\\ CO\cdot O\cdot CMe\end{matrix}.$$

Bülow and Deseniss obtained phthalylacetylacetone in 50% and 1 : 3-diketo-2-acetylhydrindene in 15—20% yield by adding phthalyl chloride (1 mol.) to an ethereal suspension of sodioacetylacetone (2 mols.) (Abstr., 1905, i, 42). The yields are 75% and 5—10% respectively when the order of the addition is reversed; the yield of diketoacetylhydrindene is increased by working at a higher temperature and by lessening the proportion of phthalyl chloride. Phthalyl chloride and ethyl sodioacetoacetate in ether react to form, in the proportions 1 : 1 or 1 : 2, the two forms, m. p. 124° and 96—97° respectively, of ethyl phthalylacetoacetate, in the proportions 1 : 3, *ethyl phthaloxydiacetoacetate*, $C_6H_4{<}\begin{matrix}C(:CAc\cdot CO_2Et)\\ C(:CAc\cdot CO_2Et)\end{matrix}{>}O$, m. p. 112°, and in the proportions 1 : 4, ethyl phthalyldiacetoacetate.

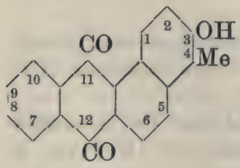
[With P. OPPERMANN.]—As an additional argument in favour of the symmetric structure of phthalyl chloride, the authors advance the fact that its ultraviolet absorption spectrum is similar to those of ethyl phthalate and *iso*phthalyl chloride. C. S.

The Methyl-1:2-benzanthraquinone Series. II. ROLAND SCHOLL and WALTHER NEUBERGER [with WALTER TRITSCH and JULIUS POTSCHIWAUSCHEG] (*Monatsh.*, 1912, 33, 507—533. Compare Scholl and Tritsch, this vol., i, 36).—Unsuccessful attempts were made to condense 2-amino-1-methylnaphthalene or its acetyl or phthaloyl derivatives with phthalic anhydride or with *o*-cyanobenzoyl chloride.

From 2-methoxy-1-methylnaphthalene, phthalic anhydride, and aluminium chloride, 2-methoxy-1-methylnaphthalene-6-phthaloylic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot C_{10}H_5Me\cdot OMe$, is obtained. This is more easily sulphonated than condensed by concentrated sulphuric acid, but the

reduction product, 6-methoxy-5-methyl-2-naphthylphenylmethane-2′-carboxylic acid, $CO_2H\cdot C_6H_4\cdot CH_2\cdot C_{10}H_5Me\cdot OMe$, was converted into 3-methoxy-4-methyl-1 : 2-benzanthraquinone,

$$C_6H_4<\substack{CO\\CO}>C_{10}H_4Me\cdot OMe.$$



This compound can be demethylated by hydrogen bromide in acetic acid to 3-hydroxy-4-methyl-1 : 2-benzanthraquinone (annexed formula), which could not, however, be converted into the corresponding amine. 2-Hydroxy-1-methylnaphthalene-6-phthaloylic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot C_{10}H_5Me\cdot OH$, prepared either from β-1-methylnaphthol, phthalic anhydride, and aluminium chloride, or from the 2-methoxy-1-methylnaphthalene-6-phthaloylic acid, is converted by Buchner's method into 2-amino-1-methyl naphthalene-6-phthaloylic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot C_{10}H_5Me\cdot NH_2$, and this by the stages 3-amino-4-methyl-1 : 2-benzanthraquinone and 3-iodo-4-methyl-1 : 2-benzanthraquinone into 1 : 1′-dimethyl-5 : 6 : 5′ : 6′-diphthaloyl-2 : 2′-dinaphthyl,

$$C_6H_4<\substack{CO\\CO}>C_{10}H_4Me\cdot C_{10}H_4Me<\substack{CO\\CO}>C_6H_4,$$

which could not be condensed to a dibenzpyranthrone.

From 3-chloro-4-methyl-1 : 2-benzanthraquinone, on fusion with potassium ethoxide, a compound,

$$C_6H_4<\substack{CO\\CO}>C_{10}H_4<\substack{CH_2\\CH_2}>C_{10}H_4<\substack{CO\\CO}>C_6H_4,$$

and a hydro-derivative are obtained.

1-*Methyl*-2-*naphthylphthalimide*, $C_6H_4<\substack{CO\\CO}>N\cdot C_{10}H_6Me$, forms crystals, m. p. 200—201°. 2-*Amino*-1-*methylnaphthalene*-N-*phthaloylic acid* is a colourless, crystalline precipitate, decomposing at 180—190° into the above phthalimide.

o-*Cyanobenzoyl chloride* separates in lustrous needles, m. p. 73°; it has a mild, aromatic odour.

2-*Methoxy*-1-*methylnaphthalene*-6-*phthaloylic acid* has m. p. 161—163°; it gives at first a brown solution in concentrated sulphuric acid, which soon becomes violet or blue.

6-*Methoxy*-5-*methyl*-2-*naphthylphenylmethane*-2′-*carboxylic acid* crystallises in colourless platelets or slender needles, m. p. 166°. In concentrated sulphuric acid the coloration is at first yellow, and then becomes red.

6-*Hydroxy*-5-*methylnaphthylphenylmethane*-2′-*carboxylic acid* forms a granular, crystalline mass sintering at 165°, m. p. 179—181°.

3-*Methoxy*-4-*methyl*-1 : 2-*benzanthraquinone* is prepared by the action of sulphuric acid on the naphthylphenylmethane derivative, whereby 3-*methoxy*-4-*methyl*-1 : 2-*benzanthrone*-9 is formed, and subsequent oxidation with chromic anhydride. It crystallises in glistening, yellowish-red or brownish-red needles, m. p. 235—236°. When oxidised with potassium permanganate, anthraquinone-1 : 2-dicarboxylic acid is obtained.

3-*Hydroxy*-4-*methyl*-1 : 2-*benzanthraquinone* crystallises in stellate

aggregates of needles, which begin to sublime at 275°, m. p. 283—284°. The solution in sodium hydroxide changes colour with increasing concentration from reddish-violet through bluish-violet and blue to bluish-green.

2-*Hydroxy*-1-*methylnaphthalene*-6-*phthaloylic acid* crystallises in small, colourless, silky platelets, m. p. 264—265°, with frothing. The coloration in concentrated sulphuric acid rapidly changes from yellowish-brown to a deep bluish-violet.

2-*Amino*-1-*methylnaphthalene*-6-*phthaloylic acid* forms lustrous, yellow, crystalline splinters; it begins to decompose into the amide at 170°, sinters at 206°, m. p. 212—213° (decomp.).

3-*Amino*-4-*methyl*-1 : 2-*benzanthraquinone* crystallises in brownish-red, prismatic platelets, which begin to sublime at 180°, m. p. 261—265° (some decomp.).

3-*Iodo*-4-*methyl*-1 : 2-*benzanthraquinone* separates in golden-yellow, long, prismatic plates, m. p. 276—277°.

1 : 1′-*Dimethyl*-5 : 6 : 5′ : 6′-*diphthaloyl*-2 : 2′-*dinaphthyl* is an insoluble, amorphous, dark yellow powder, which sinters about 360°.

E. F. A.

Aromatic Aldehydo-acids. HUGO SIMONIS [with ALFRED BOEHME and J. BENENSON] *Ber.*, 1912, **45**, 1584—1592).—I.—iso*Phthalaldehydic Acid.*—By the action of bromine on phthalaldehyde, the acid bromide of phthalaldehydic acid, $CHO\cdot C_6H_4\cdot COBr$, is obtained as an intermediate product, and undergoes internal condensation to monobromophthalide, $C_6H_4<\substack{CO \\ CHBr}>O$. This when hydrolysed yields phthalaldehydic acid. Bromine is without action on the isomeric *iso*phthalaldehyde and terephthalaldehyde at the ordinary pressure, but on heating in sealed tubes at 140° or, on a large scale, in an enamel-lined autoclave, the corresponding aldehydic acids are obtained.

*iso*Phthalaldehydic acid (compare Reinglass, Abstr., 1891, 1344) crystallises in colourless needles from water, m. p. 175°, or in glistening platelets from chloroform. The *methyl* ester, m. p. 53°, forms an *oxime*, m. p. 104°; the *ethyl* ester is a colourless liquid of agreeable odour, solidifying at −10° to large, colourless prisms, b. p. 278°, D^{18} 1·093.

The *chloride*, an oily liquid, b. p. 130°/20 mm., on treatment with dry ammonia gas in benzene yields an *amide* crystallising in colourless prisms, decomp. 190°.

The oxime, $CO_2H\cdot C_6H_4\cdot CH:N\cdot OH$, separates in colourless, microscopic needles (compare Reinglass, *loc. cit.*), m. p. 188°. On heating at this temperature, *iso*phthalamic acid is formed.

The *anil* forms stellate groups of colourless prisms, m. p. 156°. The compound with *p*-toluidine has m. p. 165°, with α-naphthylamine, m. p. 164°, and with β-naphthylamine, m. p. 210°; they all form colourless needles or plates.

The *semicarbazone* has m. p. 265°. The *phenylhydrazone* forms colourless, flat, lustrous needles, m. p. 265°.

ω-*Acetylstyrene*-m-*carboxylic acid*, $CO_2H\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH_3$, forms yellow needles which intumesce at 185°, m. p. 194—196°. The solution

in alkali hydroxide is yellow, that in concentrated sulphuric acid is brownish-red.

m-*Carboxycinnamic acid*, $CO_2H \cdot C_6H_4 \cdot CH:CH \cdot CO_2H$, prepared by heating *iso*phthalaldehydic acid with sodium acetate and acetic anhydride, has m. p. 264°.

The leuco-base of p,p′-*tetramethyldiaminotriphenylmethane*-m-*carboxylic acid*, $CO_2H \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NMe_2)_2$, from *iso*phthalaldehyde acid and dimethylaniline, crystallises in pointed, colourless prisms, m. p. 233°. On oxidation, malachite-green-*m*-carboxylic acid is obtained.

II.—*Terephthalaldehydic acid*, $COH \cdot C_6H_4 \cdot CO_2H$, crystallises in colourless, rhombic prisms or flat, streaked needles, m. p. 256°. The *methyl* ester forms stellar aggregates of colourless needles, m. p. 60°, b. p. 265°. The *ethyl* ester is a liquid. The *chloride* has b. p. 258°, and forms colourless prisms, m. p. 48°.

The *anil* forms rhombic prisms, m. p. 222°; the o-*chloroanil* separates in light yellow crystals, m. p. 217—218°; the m-*nitroanil* consists of yellow needles, m. p. 268; the p-*tolil* crystallises in lustrous, pale yellow platelets, which soften at 237°, m. p. 261—263°; the p-*acetylanil* forms pale yellow, microscopic platelets, m. p. 215° (decomp.); the *β-naphthil* forms yellow platelets, m. p. 240—241°; the isomeric *α-naphthil* gives pointed prisms, m. p. 235°.

Terephthalaldehydic acid-m-*aminoanil*, $CO_2H \cdot C_6H_4 \cdot CH:N \cdot C_6H_4 \cdot NH_2$, is a canary-yellow, granular precipitate, m. p. above 300°; it forms a diazonium salt, which couples with β-naphthol in alkaline solution to a bluish-red dye.

With *p*-phenylenediamine, yellow, microscopic prisms of 1:4-*bis*-[p-*carboxybenzylideneamino*]*benzene*, $[CO_2H \cdot C_6H_4 \cdot CH:N]_2C_6H_4$, are obtained having m. p. above 300°; analysis of the silver salt confirms the structure as a dicarboxylic acid.

Terephthalaldehydic acid azine, $CO_2H \cdot C_6H_4 \cdot CH:N \cdot N:CH \cdot C_6H_4 \cdot CO_2H$, is a bright yellow, sandy powder, m. p. above 280°.

2-*Phenylbenziminazole*-p-*carboxylic acid*,

$$C_6H_4 \genfrac{<}{>}{0pt}{}{N}{NH} C \cdot C_6H_4 \cdot CO_2H,$$

crystallises in yellow, microscopic plates or six-sided prisms.

Mandelonitrile-p-*carboxylic acid* is obtained on heating the bisulphite compound of the aldehyde acid with potassium cyanide solution. On the addition of acid, a yellow, granular precipitate is obtained, which decomposes when heated.

p-*Carboxycinnamic acid* is obtained on heating terephthalaldehyde acid with sodium acetate and acetic anhydride in a stream of carbon dioxide at 150—160°; it forms an insoluble, colourless, crystalline powder. E. F. A.

Terephthalyldicarbamide and Terephthalyldinitrodicarbamide. MICHAEL PFANNL and OTTO DAFERT (*Monatsh.*, 1912, 33, 485—505).—Terephthalyldicarbamide is prepared with a good yield by heating terephthalyl chloride with excess of carbamide. It gives no biuret reaction, and is remarkably stable towards acids, 96% sulphuric acid only hydrolysing it above 55°. It is also resistant to ring formation, and when heated in a stream of hydrogen chloride in a

vacuum it is degraded only to nitrile. It is colourless and amorphous, subliming above 200° (decomp.).

Terephthalyldinitrodicarbamide, $C_6H_4(CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NO_2)_2$, is remarkable in containing two labile nitroamine groups in the molecule. It is decomposed by water in a manner analogous to nitrocarbamide, forming amine, carbon dioxide, water, and nitrous oxide. There is no difference in colour between the sodium salt and the acid; they possibly exist in tautomeric modifications,. The *sodium* salt crystallises in colourless, stellar aggregates of needles; the *free acid* is colourless, and explodes when heated. E. F. A.

Tannin. KARL FEIST (*Ber.*, 1912, **45**, 1493—1494).—The author points out that he has demonstrated the glucosidic nature of tannin previous to the work of Fischer and Freudenberg (this vol., i, 471). H. W.

Constitution of Tannin. RODGER J. MANNING and MAXIMILIAN NIERENSTEIN (*Ber.*, 1912, **45**, 1546—1551. Compare this vol., i, 468).—Manning has shown (Abstr., 1910, i, 851) that tannin on esterification forms two pentaethyl esters of pentagallolylglucoside; this behaviour is not in agreement with the constitution ascribed to tannin by Fischer and Freudenberg (this vol., i, 471). Tannin (Schering) yields only ethyl gallate when esterified and no sugar. The change in rotation of tannin solutions on boiling in a stream of hydrogen has been followed, measurements being made also of the tannin and non-tannin matter present. In twelve hours the rotation falls from $[\alpha]_D$ +68·22° to +59·84°, the amount of tannin falls from 0·4274 to 0·3986, and the amount of non-tannin rises from 0·0244 to 0·0532; it is always optically inactive, which excludes the possibility of dextrose being eliminated. E. F. A.

The Behaviour of Acetonylacetone towards β-Dialdehydes. WILLIAM J. HALE (*Ber.*, 1912, **45**, 1596—1603. Compare Abstr., 1908, i, 634).—The condensation of acetonylacetone with nitromalonaldehyde in presence of small quantities of sodium hydroxide yields some 4-nitro-2-acetonylphenol, but also four times as much of a second product. The possibility of this being a diphenol was previously discredited by the fact that nitroacetonylphenol and nitromalonaldehyde only condense in excess of alkali or piperidine, and a second supposition, that the nitroacetonylphenol itself undergoes condensation to a cumarone derivative, is now shown to be improbable, for such a change can only be brought about by means of sulphuric acid or zinc chloride. Since the reaction takes place between equimolecular proportions, there remains the explanation that the two aldehyde groups condense with the two methylene groups, producing 5-nitro-2:3-diacetyl*cyclo*pentadiene, and this substance is actually obtained on adding hydrochloric acid to the mother liquor after the acetonylnitrophenol has been precipitated by carbon dioxide.

5-*Nitro*-2:3-*diacetyl*cyclo*pentadiene*, $NO_2{\cdot}C_5H_3(COMe)_2$, is a faintly coloured substance, crystallising from ethyl acetate in glistening needles, m. p. 195°. It is fairly acid, does not absorb bromine, but

is readily attacked by permanganate or concentrated nitric acid. 4-*Nitro*-1-*methylcumarone*, $NO_2\cdot C_8H_4OMe$, is obtained quantitatively from 4-nitro-2-acetonylphenol by condensation with zinc chloride in glacial acetic acid (compare Stoermer, Abstr., 1900, i, 650). It separates in short needles, m. p. 97°, from diluted alcohol, gives a deep red solution in sulphuric acid, and is converted by nitric acid into 4 : 6-*dinitro*-1-*methylcumarone*, $C_8H_3OMe(NO_2)_2$, which may also be obtained from 4 : 6-dinitro-2-acetonylphenol (Abstr., 1908, i, 634) in colourless needles, m. p. 165°. Improvements in the production of acetonylphenols will render this cumarone synthesis valuable.

J. C. W.

Oxalyl Chloride. IV. The Friedel and Crafts' Reaction with Oxalyl Chloride and Oxalyl Bromide. HERMANN STAUDINGER [with E. ANTHES and MAX SCHÖLLER (*Ber.*, 1912, **45**, 1594—1596).—The action of oxalyl chloride on aromatic hydrocarbons under the influence of aluminium chloride results usually in the formation of mono-ketones (compare Abstr., 1909, i, 905), but Liebermann has shown that some highly reactive aromatic compounds produce the expected diketones (compare Abstr., 1911, i, 656). This is explained by the fact that the decomposition of oxalyl chloride by aluminium chloride into carbonyl chloride and carbon monoxide takes place more slowly than the condensation with these reactive substances, and in support of this view it is shown that anisole is converted into anisil, and that in the presence of carbon monoxide under a pressure of 150 atmospheres, dimethylaniline can be converted into tetramethyldiaminobenzil.

Oxalyl bromide, b. p. 103—105°, which will be described in a future paper, decomposes most easily in presence of aluminium chloride into bromine and carbon monoxide, but it condenses even more readily with benzene, so that benzil may be obtained and not merely benzophenone or bromobenzenes. It seems, therefore, more suitable than the chloride for the preparation of diketones. J. C. W.

Bromination of *cyclo*Hexanone and *cyclo*Hexanol. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1912, **154**, 1509—1511*).—The tetrabromo-derivative obtained by the action of bromine in the presence of aluminium bromide on *cyclo*hexanone (compare Abstr., 1911, i, 779) is identical with that obtained by Wallach (*Annalen*, 1905, **343**, 133). It is, however, best prepared by the action of bromine in carbon tetrachloride solution. The liquid obtained by its decomposition on heating to 120—125° is a mixture of several monobromophenols and 2 : 6-dibromophenol.

*cyclo*Hexanol when treated with bromine in carbon tetrachloride yields tetrabromo*cyclo*hexanone and dibromo*cyclo*hexane. Temperature and duration of the reaction do not affect the result. Bromine in boiling acetic acid converts both the ketone and the alcohol into 2 : 4 : 6-tribromophenol. W. G.

Terpenes and Ethereal Oils. CIX. OTTO WALLACH (*Annalen*, 1912, **389**, 169—184).—[With WALTHER OST.]—*cyclo*Hexyl-2-*cyclo*-

* and *Bull. Soc. chim.*, 1912, [iv], **11**, 658—665.

hexanonoxime (Abstr., 1911, i, 473), unlike methyl-3-*cyclo*hexanonoxime (Abstr., 1906, i, 514), yields by treatment with diluted sulphuric acid ($5:1H_2O$) on the water-bath for five minutes only one iso-*oxime*, $C_6H_{11}\cdot CH<\begin{matrix}NH-CO-CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}$, m. p. 145—146°, which is converted by 25% hydrochloric acid at 130—140° into *ε-amino-ε*-cyclo*hexylhexoic acid*, $C_6H_{11}\cdot CH(NH_2)\cdot[CH_2]_4\cdot CO_2H$, m. p. 203° (decomp.) (*benzoyl* derivative, m. p. 228°). By oxidation with 5% potassium permanganate in faintly alkaline solution, the amino-acid yields δ-hexahydrobenzoylvaleric acid, identical with that obtained by the direct oxidation of *cyclo*hexyl-2-*cyclo*hexanone (*loc. cit.*). The constitution of this ketonic acid is definitely proved by treating an ethereal solution of its oxime with phosphorus pentachloride, whereby the isomeric *amide*, $C_6H_{11}\cdot NH\cdot CO\cdot[CH_2]_4\cdot CO_2H$, m. p. 133—134°, is produced, which is hydrolysed to *cyclo*hexylamine and adipic acid by 25% hydrochloric acid at 140°. The reduction of δ-hexahydrobenzoylvaleric acid by sodium and boiling alcohol yields, after purification of the product by distillation in a vacuum, the *lactone*,

$$C_6H_{11}\cdot CH<\begin{matrix}O\text{———}\\ [CH_2]_4\end{matrix}>CO,$$

m. p. 56°, b. p. 175°/12 mm., of *ε-hydroxy-ε*-cyclo*hexylhexoic acid*. The hydroxy-acid itself, which is an oil and is also obtained by the action of nitrous acid on ε-amino-ε-*cyclo*hexylhexoic acid, is converted by boiling dilute sulphuric acid into an unsaturated *acid*, $C_{12}H_{20}O_2$, b. p. 182—186°/20 mm. This acid, which is more easily obtained from the preceding lactone and boiling dilute sulphuric acid, is oxidised to δ-hexahydrobenzoylvaleric acid by successive treatment with faintly alkaline 2% potassium permanganate and with chromic and sulphuric acids.

The dicyclic ketone obtained by the auto-condensation of 1-methyl-3-*cyclo*hexanone is reduced by Paal's method to *dimethyldi*cyclo*hexylhexanone*, $C_{14}H_{24}O$, b. p. 146—148°/12 mm., which forms a *semicarbazone*, m. p. 163°, and an *oxime*, m. p. 95—96°, and yields by oxidation a *ketonic acid*, b. p. 222—225°/14 mm. (*silver* salt, $C_{14}H_{23}O_3Ag$; *semicarbazone*, m. p. 169—171°).

*cyclo*Pentene-2-*cyclo*pentanone is reduced quantitatively by Paal's method to *cyclo*pentyl-2-*cyclo*pentanone (Godchot and Taboury, Abstr., 1911, i, 385), b. p. 232—233°, D^{21} 0·9745, n_D 1·4763 (*oxime*, m. p. 78—79°, and its *hydrochloride*, m. p. 112—113°), which forms a *benzylidene* derivative, m. p. 97—98°, and is oxidised by chromic acid to *δ-keto-δ*-cyclo*pentylvaleric acid*, $C_5H_9\cdot CO\cdot[CH_2]_3\cdot CO_2H$ (*semicarbazone*, m. p. 181—183°). This oily acid is also readily obtained by oxidising *cyclo*pentyl-2-*cyclo*pentanone with cold 2% potassium permanganate.

2-cyclo*Pentyl*cyclo*pentanol*, $C_5H_9\cdot C_5H_8\cdot OH$, b. p. 235—236°, D^{17} 0·9785, n_D^{17} 1·4884 (*phenylurethane*, m. p. 88—89°), obtained by reducing *cyclo*pentyl-2-*cyclo*pentanone by sodium and alcohol, is converted by zinc chloride at 150° into cyclo*pentyl*-Δ′-cyclo*pentene*, $C_5H_9\cdot C_5H_7$, b. p. 196·5—198°, $D^{19·5}$ 0·9080, $n_D^{19·5}$ 1·4938, which forms a *nitrosochloride*, m. p. 113—114°.

The yellow 1 : 3-di*cyclo*pentene-2-*cyclo*pentanone, which is obtained in 12—13% yield by the action of alcoholic sodium ethoxide on *cyclo*-

pentanone, is reduced by Paal's method to 1 : 3-*dicyclopentyl*-2-*cyclopentanone*, $C_5H_9\cdot C_5H_6O\cdot C_5H_9$, which is colourless, has b. p. 165—170°/12 mm., D^{19} 0·9925, and n_D^{19} 1·4956, forms a *semicarbazone*, m. p. 188—190°, and an *oxime*, m. p. 85—86°, and is oxidised by chromic acid to *δ-keto-αδ-dicyclopentylvaleric acid*,

$$C_5H_9\cdot CO\cdot CH_2\cdot CH_2\cdot CH(C_5H_9)\cdot CO_2H$$

(*semicarbazone*, m. p. 195—196°).

2 : 5-*Dicyclopentylcyclopentanol*, $C_5H_9\cdot C_5H_6(OH)\cdot C_5H_9$, m. p. 68°, b. p. 210°/100 mm., obtained by reducing the di*cyclo*pentyl*cyclo*pentanone by sodium and alcohol, is converted into 1 : 3-*dicyclopentyl*-Δ'-*cyclopentene*, b. p. 210°/100 mm., D^{20} 0·939, n_D^{20} 1·5065, by zinc chloride at 150—200°. C. S.

Terpenes and Ethereal Oils. CX. OTTO WALLACH (*Annalen*, 1912, **389**, 185—198).—[With WALTHER OST.]—In accordance with expectation, nitrosopinene in methyl alcohol is reduced by hydrogen in the presence of a little colloidal palladium, the addition of hydrogen occurring at the ethylenic linking. However, the product is not pinocamphonoxime itself, but a stereoisomeric *pinocamphonoxime*, m. p. 87°; the ketone obtained by its hydrolysis by acids yields a semicarbazone and an oxime identical with those from pinocamphone. When pinocarveol (from pinylamine) is reduced by Paal's method and the resulting saturated alcohol is oxidised, the ketone obtained yields an oxime and a semicarbazone identical with those of pinocamphone. It follows, therefore, that pinene, pinocarvone, carvopinone, and pinocamphone are mutually related as represented by the formulæ previously ascribed to these substances by the author.

[With WALTER N. HAWORTH.]—It has already been shown that the halogen in the nitrosochlorides of unsaturated hydrocarbons can be replaced by the acetoxy-group (Abstr., 1910, i, 569) and that the nitrosochlorides can be reduced directly to saturated bases and ketones by zinc and acetic acid (Abstr., 1911, i, 469). These processes have now been applied in the following cases. Ethylidene*cyclo*hexane nitrosochloride, m. p. 132° (Abstr., 1908, i, 402), is converted by sodium acetate and glacial acetic acid at 60—65° into the *oxime* of 1-*acetoxycyclohexyl methyl ketone*, $OAc\cdot C_6H_{10}\cdot CMe\colon NOH$, m. p. 103°, the hydrolysis of which by 2% sulphuric acid yields Δ^1-tetrahydroacetophenone and 1-*hydroxycyclohexyl methyl ketone*,

$$OH\cdot C_6H_{10}\cdot COMe,$$

b. p. 125—126°/50 mm. (*semicarbazone*, m. p. 196°). The reduction of ethylidene*cyclo*hexane nitrosochloride by zinc and acetic acid yields hexahydroacetophenone and *α-cyclohexylethylamine*, $C_6H_{11}\cdot CHMe\cdot NH_2$ (*platinichloride*, $2C_8H_{17}N,H_2PtCl_6$, m. p. 218° [decomp.]).

The reduction of 1-methyl-3-ethylidene*cyclo*hexane by zinc and acetic acid yields a base (unexamined) and 1-*methylcyclohexyl methyl ketone*, $C_6H_{10}Me\cdot COMe$, b. p. 196—197° (*semicarbazone*, m. p. 180—181°).

[With MAX BEHNKE.]—When heated with potassium hydroxide, monocyclic ketones tend to form condensation products (Abstr., 1909, i, 811); their oximes, however, undergo fission of the ring; thus menthoneoxime and potassium hydroxide, heated at 220° for thirty-

six hours in an autoclave, yield ammonia, thymol, $\beta\zeta$-dimethyloctoic acid, $CHMe_2\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CO_2H$ (Abstr., 1897, i, 428), and lower fatty acids. The decoic acid forms a *methyl* ester, b. p. 212—215°, *amyl* ester, b. p. 265—266°, *chloride*, b. p. 106—109°/20 mm. (*anilide*, m. p. 91—92°), and *amide*, m. p. 108—109°, from which is prepared the *nitrile*, b. p. 220—225°, D^{21} 0·821, n_D^{21} 1·4276. By reduction, the nitrile yields $\gamma\eta$-*dimethyloctylamine*,

$$CHMe_2\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CH_2\cdot NH_2,$$

b. p. 202—203°, D^{21} 0·791, n_D^{21} 1·4316, which forms a *phenylthiocarbamide*, m. p. 78—79°, and *oxamide*, m. p. 76—77°, and is converted by nitrous acid into $\gamma\eta$-*dimethyloctyl alcohol*, b. p. 100—102°/13 mm., and a *decylene*, $C_{10}H_{20}$, b. p. 152—155°, D^{19} 0·744, n_D^{19} 1·4213. C. S.

Action of Sodamide and Alkyl Halides on Benzoyl*cyclo*propane. ALBIN HALLER and EUGÉNE BENOIST (*Compt. rend.*, 1912, **154**, 1567—1570).—An investigation for the comparison of the behaviour of ketones containing a trimethylene ring with that of ordinary ketones.

Ethyl benzoyl*cyclo*propanecarboxylate (*oxime*, m. p. 152°: Perkin, Trans., 1885, **47**, 840) is converted successively into the corresponding acid and benzoyl*cyclo*propane (oxime, m. p. 95—96°).

A more convenient method of preparation is by the series of changes trimethylene chlorobromide$\longrightarrow$trimethylene chlorocyanide$\longrightarrow$*cyclo*propanecarboxylonitrile$\longrightarrow$*cyclo*propanecarboxylic acid ; the acid (b. p. 181—182°/760 mm.) is converted by thionyl chloride into the acid chloride, which condenses with benzene in the presence of aluminium chloride, giving benzoyl*cyclo*propane.

When warmed with sodamide in dried benzene, benzoyl*cyclo*propane gives a sodium derivative, but in moist benzene, *cyclo*propane is evolved and benzamide remains. When sodium benzoyl*cyclo*propane is treated in warm benzene with methyl iodide, 1-*benzoyl*-1-*methyl*cyclo*propane*, $COPh\cdot CMe{<}{\begin{matrix}CH_2\\|\\CH_2\end{matrix}}$, is obtained, b. p. 127—128°/18 mm.; *oxime*, m. p. 115° (decomp.) ; p-*nitrophenylhydrazone*, orange leaflets, m. p. 112°. From these properties the substance is evidently distinct from that obtained by Blaise and Herman (Abstr., 1911, i, 881) ; when warmed with sodamide and benzene, methyl*cyclo*propane and benzamide are obtained.

1-*Benzoyl*-1-*allyl*cyclo*propane*, obtained in an analogous manner to the above methyl compound, has b. p. 136—137°/16 mm. ; a mixture of sodamide and benzene is without effect on this substance.

1-*Benzoyl*-1-*benzyl*cyclo*propane*, b. p. 203—204°/20 mm., crystallises in tablets, m. p. 33·5° ; when heated with sodamide and moist benzene it undergoes scission into benzene and the *amide* of *benzyl*cyclo*propanecarboxylic acid* (m. p. 84°), which is easily hydrolysed to the corresponding free *acid* (cubes, m. p. 103°).

Oxidation of benzoylbenzyl*cyclo*propane by chromium trioxide in acetic acid solution gives a *substance*, $C_{17}H_{14}O_2$, possibly a dibenzoyl*cyclo*propane, crystallising in cubes, m. p. 87—88°.

The refractivities of benzoyl*cyclo*propane, together with its methyl and benzyl derivatives, and ethyl benzoyl*cyclo*propanecarboxylate,

are given for the α-, *D*-, β-, and γ-lines. The results with the *D*-line indicate that in these substances the trimethylene ring exerts a similar effect to an ethylenic linking in causing exaltation when conjugated with a ketonic group. D. F. T.

mm'-Dinitrobenzil. HEINRICH KLINGER and WALTER MARTINOFF (*Annalen*, 1912, **389**, 232—237).—By treatment with colourless nitric acid, D 1·53, at −10°, benzil is converted into mm'-*dinitrobenzil*, m. p. 108·5—109°, yellow needles. Attempts to convert it into dinitrobenzilic acid by the hydroxide of potassium, sodium, or barium have been unsuccessful. It is converted into *m*-nitrobenzoic acid by boiling water and silver oxide. C. S.

Correction Concerning the Formation of Cyananilic Acid. M. M. RICHTER (*Ber.*, 1912, **45**, 1682. Compare this vol., i, 34).—The formation of a very small amount of "cyananilic acid" from chloranilic acid was due to the presence of a little chloranil. J. C. W.

Abnormal Behaviour of Some Anthraquinone Derivatives towards Alkaline Reducing Agents. I. CHRISTIAN SEER [with E. KARL] (*Monatsh.*, 1912, **33**, 535—548).—Most anthraquinone derivatives when warmed with alkaline reducing agents yield characteristic coloured solutions. Certain substituting groups attached near the carbonyl groups cause steric hindrance and render the compound indifferent to alkaline reducing agents; thus 1 : 3 : 5 : 7-tetramethylanthraquinone is quite indifferent, but anthraquinone-1 : 3 : 5 : 7-tetracarboxylic acid obtained from it on oxidation, gives an intense violet-red on reduction.

Further substitution in 1 : 3 : 5 : 7-tetramethyl anthraquinone, producing 4 : 8-dinitro- and 2 : 4 : 6 : 8-tetranitro-derivatives, still results in compounds which are almost indifferent to alkaline reducing agents. In these compounds, also, the nitro-groups are reduced to amino-groups only with difficulty.

1 : 5-Dibenzylaminoanthraquinone is equally resistant, but the compound formed on substituting the remaining hydrogen of the amino-group by the benzoyl radicle gives a red solution with alkaline reducing agents, the negative residues evidently acting to restore the activity of the carbonyl groups.

1 : 4-Dimethylanthraquinone gives a red solution on reduction; 1-methyl-4-*p*-tolylanthraquinone is, however, indifferent.

4 : 4'-Dimethyldiphenyl-3-phthaloylic acid is not converted into the anthraquinone derivative by condensation by means of sulphuric acid, zinc chloride, or phosphorus pentachloride. The reduction product, 5-*p*-tolyl-2-methyldiphenylmethane-2'-carboxylic acid, is converted by means of zinc chloride into 1-methyl-4-*p*-tolylanthrone, from which the desired 1-methyl-4-*p*-tolylanthraquinone is obtained on oxidation with chromium trioxide.

Oxidation with ferric chloride converts the above anthrone into 1 : 1'-dimethyl-4 : 4'-di-*p*-tolyldianthrone-10 : 10'. An additional product of oxidation with chromium trioxide is a small quantity of 4-*p*-carboxyphenylanthraquinone-1-carboxylic acid. When a large

excess of the oxidising agent is used, the methyl groups are oxidised to carboxyl, but action proceeds beyond the dicarboxylic acid, and the benzene ring is opened with the formation of a mixture of 4-*p*-carboxylphenylanthraquinone-1-carboxylic acid and anthraquinone-1 : 4-dicarboxylic acid as the final result. The dicarboxylic acid gives a dark red coloration with alkaline reducing agents.

5-p-*Tolyl-2-methyldiphenylmethane-2′-carboxylic acid*,

$$CO_2H \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot C_6H_4Me,$$

crystallises in stellar aggregates of colourless needles, m. p. 163—164°. The solution in concentrated sulphuric acid is yellow, becoming reddish-violet when kept.

1-*Methyl*-4-p-*tolylanthrone*-10, $C_6H_4<{CH_2 \atop CO}>C_6H_3Me \cdot C_6H_4Me$, forms pale yellow, long prisms, m. p. 145—146°, dissolving in concentrated sulphuric acid with a reddish-brown coloration.

1 : 1′-*Dimethyl*-4 : 4′-*di*-p-*tolyl*-9 : 9′-*dianthrone*-10 : 10′,

$$CO<{C_6H_4 \text{———————} \atop C_6H_2Me(C_6H_4Me)}>CH<{\text{———————} C_6H_4 \atop C_6H_2Me(C_6H_4Me)}>CO,$$

crystallises in colourless, glistening, prismatic platelets, m. p. 237°.

1-*Methyl*-4-p-*tolylanthraquinone*, $C_6H_4<{CO \atop CO}>C_6H_2Me \cdot C_6H_4Me$, crystallises in yellow needles, m. p. 212°; the coloration with concentrated sulphuric acid is red.

4-p-*Carboxyphenylanthraquinone*-1-*carboxylic acid*,

$$C_6H_4<{CO \atop CO}>C_6H_2(CO_2H) \cdot C_6H_4 \cdot CO_2H,$$

forms pale yellow, microscopic needles, soluble in concentrated sulphuric acid with a golden-yellow coloration. E. F. A.

Binary Mixtures Containing Camphor. JOUNIAUX (*Bull. Soc. chim.*, 1912, [iv], 11, 546—552).—Camphor forms liquid mixtures with naphthalene, α-nitronaphthalene, β-naphthylamine, pyrogallol, and benzoic acid, and the behaviour of the camphor–naphthalene mixture on cooling has been described already (this vol., i, 198). Binary mixtures with each of the four other substances mentioned behave similarly, and a general curve and tables illustrating this behaviour are given in the original.

The eutectic mixtures have the following molecular compositions, %: α-nitronaphthalene 46, β-naphthylamine 36, pyrogallol 31 (m p. 21°), benzoic acid 37 (m. p. 27·2°), the rest being camphor. In all four cases the first crystals, which separate on cooling, consist of camphor, so long as the second constituent does not form more than 30 mols. % of the mixture. The addition of even very minute quantities of the second constituent causes a remarkable lowering in the temperature of commencing solidification.

T. A. H.

Pinene and Camphor. MARIO MAYER (*Chem. Zentr.*, 1912, i, 1312; from *Habilitationschr.*, Florence, 1911, 61 pp.).—By fractional crystallisation of *i*-α-pinenehydroxylamineoxime α-bromo-π-camphorsulphonate the author has separated the salt into three fractions, from

which the three corresponding bases have been prepared by treatment with sodium carbonate. The constants of these six substances are as follows: (1) *salt*, m. p. 195° (decomp.), $[\alpha]_D + 79°$: *base*, m. p. 147° (decomp.), $[\alpha]_D + 60·5°$; (2) *salt*, m. p. 172° (decomp.), $[\alpha]_D + 39°$: *base*, m. p. 145° (decomp.), $[\alpha]_D - 59·6°$; (3) *salt*, m. p. 175° (decomp.), $[\alpha]_D + 52°$: *base*, m. p. 140° (decomp.), $[\alpha]_D$ 0°.

Theoretically the hydroxylamineoxime should exist in four optically active forms, and the author suggests that the two optically active forms described above may be mixtures. A full discussion of the stereochemistry of pinene is given in the original. T. A. H.

Constitution of 3-Methylpulegene (3-Methylmenthadiene). Hans Rupe, Heinz Schobel, and Erwin Abegg (*Ber.*, 1912, **45**, 1528—1540).—Various formulæ have been assigned to 3-methylpulegene by Grignard, Rupe and Emmerich (Abstr., 1908, i, 556) and, by Auwers and Eisenlohr (Abstr., 1910, ii, 365, 367). On oxidation with ozone, a moderately viscid, greenish-yellow oil is obtained, which analysis indicates to be a mixture of much diozonide with a little mono-ozonide. Hydrolysis with water yields acetone in small quantities and an oil, b. p. 171°/14 mm., which is characterised as a ketonic acid; it yields a semicarbazone crystallising in slender, colourless needles, m. p. 150°. On oxidation of this acid with sodium hypobromite, β-methyl-adipic acid is obtained, whilst on oxidation with nitric acid, α-methyl-glutaric acid is formed. This behaviour establishes the constitution of the acid as δ-acetyl-γ-methylvaleric acid,

$$CH_3·CO·CH_2·CHMe·CH_2·CH_2·CO_2H,$$

but it does not enable any decision to be made between the alternative formulæ for methylpulegene.

A further product of the oxidation with ozone is a soluble brown oil, which distils at 130—140° as a viscid, yellow, odourless oil; this has the properties of an aldehyde, $C_8H_{14}O_2$, and forms a *semicarbazone*, $C_{11}H_{21}ON_3$, crystallising in colourless platelets, m. p. 266°. On oxidation of the aldehyde with potassium permanganate, it is converted into the ketonic acid.

3-*Methylpulegol*, obtained as a by-product in the preparation of methylpulegene, has b. p. 93—94°/10·5 mm., and constitutes a colourless, mobile oil with an odour of menthone.

Methylmenthone (*homomenthone*), a further by-product of the preparation of the hydrocarbon, has b. p. 94—97°/15 mm.; the *semicarbazone* crystallises in lustrous, colourless needles, m. p. 186°. The ketone prepared from this has b. p. 93°/11 mm., D_4^{20} 0·905, n_D^{20} 1·4642, $[\alpha]_D^{20}$ +43·98°. E. F. A.

The Constituents of Essential Oils. Chemical Identity of Synthetic and Natural Cedrene. Friedrich W. Semmler and K. E. Spornitz (*Ber.*, 1912, **45**, 1553—1557. Compare Semmler and Mayer, this vol., i, 366).—Natural cedrene has a somewhat higher boiling point and considerably lower optical activity than the synthetic product, and the identity of the two compounds has not been established previously. On oxidation of synthetic cedrene with ozone, the methylketonic acid formed is similar to the acid obtained in the

same way from natural cedrene, and is converted into identically the same cedrenedicarboxylic acid. Natural cedrene evidently contains other isomeric sesquiterpenes in addition to the strongly lævorotatory cedrene. E. F. A.

Essential Oils. III. Basil Oil. GUSTAVE LALOUE (*Bull. Soc. chim.*, 1912, [iv], 11, 491—494).—The author has compared the basil oils obtained from the following four varieties of *Ocimum basilicum*, cultivated near Grasse: var. *thyrsiflorum*, Benth., var. *purpurascens*, Benth., var. *album*, Benth., and var. *crispum*, E. G. Camus. These furnished respectively 0·0855, 0·0370, 0·0780, and 0·1285% of oil, so that the fourth is the best for cultivation. The four oils yielded respectively 35·19, 38·46, 39·66, and 35·19% of total alcohols, calculated as linalool, and their constants, which are tabulated in the original, showed very little variation. The amount of methoxyl in all four oils corresponded with about 55% of estragole. T. A. H.

Oil of the Southern Cypress. ALLAN F. ODELL (*J. Amer. Chem. Soc.*, 1912, 34, 824—826).—In an earlier paper (Abstr., 1911, i, 548) it was shown that the wood of the cypress (*Taxodium distichum*) contains an aldehyde. With a view to obtaining larger quantities of this compound, an examination has been made of the volatile oil of the cones. It has been found, however, that the oil does not contain any aldehydes.

Cones collected in September yielded about 1% of a yellowish-green oil with an odour of pinene, D 0·86, and α_D +18° in a 100 mm. tube. Those collected later in the year furnished $1\frac{1}{2}$—2% of an oil of darker colour and citron-like odour, with D 0·85 and α_D +35·5° in a 100 mm. tube. The composition of the oil was found to be approximately as follows: *d*-pinene, 85%; *d*-limonene, 5%; a ψ-terpene alcohol (probably sabinol), 2%; carvone, 3%; a tricyclic sesquiterpene, 3%; the remainder consisted of substances of b. p. above 275°.

E. G.

The Oil of Douglas Fir. H. K. BENSON and MARC DARRIN (*J. Ind. Eng. Chem.*, 1911, 3, 818—820).—A preliminary investigation of the nature and properties of the clear, viscous, yellow oil which is left after removal of the turpentine from the distillation products of Douglas fir. The oil was fractionated, and the constants of each fraction noted and compared (as were those of the crude oil) with the constants of pine oil as recorded by Teeple (Abstr., 1908, i, 355) and Walker (*Mass. Inst. Tech. Bull.*, Sept. 1905). From the result of this and numerous chemical tests which were also applied, the authors consider that not less than one-third of fir oil consists of turpineol, and that it closely resembles pine oil in its properties. F. M. G. M.

New Synthetic Glucosides. FERDINAND MAUTHNER (*J. pr. Chem.*, 1912, [ii], 85, 564—568).—*Tetra-acetogluco*-p-*hydroxyacetophenone*, $C_{22}H_{26}O_{11}$, prepared by shaking a solution of *p*-hydroxyacetophenone in aqueous sodium hydroxide with an ethereal solution of β-acetobromoglucose, crystallises from methyl alcohol in colourless needles, m. p.

172—173°, and is hydrolysed by aqueous barium hydroxide to *gluco*-p-*hydroxyacetophenone*, $C_{14}H_{18}O_7$, which forms colourless needles, m. p. 195—196°, and has $[\alpha]_D^{23}$ $-87{\cdot}82°$ in aqueous solution.

Tetra-acetogluco-p-*hydroxybenzaldehyde*, $C_{21}H_{24}O_{11}$, prepared in a similar manner, forms colourless needles, m. p. 144—145°, and is hydrolysed to *gluco*-p-*hydroxybenzaldehyde*, $C_{13}H_{16}O_7$, which has m. p. 157—158°, and $[\alpha]_D^{21}$ $-94{\cdot}45°$ in aqueous solution. F. B.

The Relation of Members of the Digitalin Group towards Enzymes. ARNOLD HOLSTE (*Arch. exp. Path. Pharm.*, 1912, 68, 323—332).—The various members of the digitalin group are all more or less affected by digestive enzymes, also by diastase and emulsin, being thus rendered inactive. The most resistant towards pancreatin are oleandrin, digitoxin, and strophanthin. Helleborein is easily affected. A good deal of the uncertainty of digitalis therapeutics depends on these facts. W. D. H.

Sphingosine. PHŒBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 11, 547—554).—A full account of work the results of which have already been described (this vol., i, 284). W. D. H.

Bilirubic Acid, a New Degradation Product of Bilirubin. HANS FISCHER and HEINRICH RÖSE (*Ber.*, 1912, 45, 1579—1583).—On reduction of bilirubin with hydrogen iodide and acetic acid, a crystall ne acid, $C_{17}H_{24}O_3N_2$, is obtained. It forms bunches of macroscopic platelets, m. p. 187°. It is very stable, is monobasic, and shows no pyrrole reaction. It is very resistant towards 70% sulphuric acid and towards hydriodic acid and red phosphorus at 125°. On oxidation, methyl ethylmaleinimide and hæmatic acid are obtained. The constitution

$$\mathrm{CMe}\Big\langle\begin{array}{l}\mathrm{CMe{\cdot}CEt}\quad\ \mathrm{CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}C{\cdot}CMe}\\ \mathrm{NH{-}C}\text{————}\mathrm{O}\text{————}\mathrm{C{-}NH}\end{array}\Big\rangle\mathrm{CMe}$$

is assigned to bilirubic acid for the following reasons: the degradation product shows it to contain two pyrrole rings in which the position of the β-substituting groups is fixed. It is obviously a tetra-substituted pyrrole, since it gives a negative reaction with dimethylaminobenzaldehyde and no pyrrole reaction or azo-dye. Accordingly, the four hydrogen atoms in the α-position to nitrogen must be substituted, for which purpose there are two methyl groups and oxygen available; it is assumed that the two pyrrole groups are united through oxygen. This is in agreement with the resistance to hydrogen iodide.

Hemibilirubin yields 20% of the new acid; compound II gives 9%. The yield of methylethylmaleinimide on oxidation of hemibilirubin is about half that from bilirubic acid. A by-product in the preparation of bilirubic acid from hemibilirubin and compound II is a pyrrole carboxylic acid which couples with diazobenzenesulphonic acid.

E. F. A.

Conversion of Oxindole into 2-Ketodihydro-1-thionaphthen. ("Thio-oxindole"). CHARLES MARSCHALK (*Ber.*, 1912, 45, 1481—1485. Compare this vol., i, 303).—*o*-Thiolphenylacetic acid has been transformed by distillation into 2-ketodihydro-1-thionaphthen.

The latter condenses with *p*-dimethylaminobenzaldehyde and with *a*-isatinanilide with the formation of dyes.

o-*Thiocyanophenylacetic acid*, m. p. 105—106°, was obtained by the addition of a solution of *o*-diazophenylacetic acid to a warm solution of cuprous and potassium thiocyanates. When dissolved in sodium hydroxide, mixed with sodium sulphide and evaporated to dryness, it yielded, after acidification, o-*thiolphenylacetic acid*, m. p. 96—97°, which was, however, more readily prepared by the addition of a solution of *o*-diazophenylacetic acid to a cold solution of potassium xanthate and subsequent warming of the compound so formed with potassium hydroxide solution and liberation of *o*-thiolphenylacetic acid by means of hydrochloric acid. When heated, it formed 2-*ketodihydro*-1-*thionaphthen*, a yellow oil, b. p. 260—264°/733 mm., which solidified when cooled. This was insoluble in cold sodium carbonate solution, but dissolved in hot sodium hydroxide with the formation of the *sodium* salt of *o*-thiolphenylacetic acid. It condensed with *p*-dimethylaminobenzaldehyde in methyl alcoholic solution in the presence of piperidine with formation of 3-p-*dimethylaminobenzylidene*-2-*ketothionaphthen*, m. p. 164—165°, which dyes wool and silk an orange colour in an acid-bath. When boiled with acetic anhydride and *a*-isatinanilide, thio-oxindole formed 2′-indoxyl-3-thionaphthen-2′-one (compare Bezdzik and Friedländer, Abstr., 1908, i, 673). H. W.

Scopolamine. RICHARD WILLSTÄTTER and ERNST HUG (*Zeitsch. physiol. Chem.*, 1912, **79**, 146—163).—It is supposed generally that scopolamine undergoes changes on keeping, such as racemisation, so that the optical activity vanishes, hydrolysis of the ester group, conversion into an *apo*-compound analogous to *apo*atropine, or hydrolysis of the oxide group. Experiments made to test these points prove that scopolamine remains unchanged both in physical and chemical characteristics on keeping, and that probably also the physiological action does not alter.

The alkaloid remains saturated when either atropine or scopoline is mixed with concentrated sulphuric acid, and it is stable towards bromine or permanganate on dilution. When the solution, however, is made neutral, *apo*atropine or *apo*scopolamine are obtained quantitatively.

When the solution in concentrated sulphuric acid is diluted and neutralised with ammonia, the sulphuric acid ester of the alkaloid separates. It is an internal salt of the composition

$$SO_2\begin{cases} O\text{——}CH_2\cdot CHPh \\ O\cdot NH\cdot O\cdot C_8H_{12}\cdot O \end{cases}CO.$$

*apo*Scopolamine can also be obtained by means of hydrogen chloride. On treatment of scopolamine with thionyl chloride or phosphorus pentachloride, the alcoholic hydroxyl is replaced by chlorine, and scopoleine of chlorohydrotropic acid is obtained. This is stable in acid solution, but when isolated and the ethereal solution evaporated, isomeric change takes place and *apo*scopolamine hydrochloride is obtained.

*apo*Scopolamine sulphate gives in aqueous solution with bromine

only a flocculent precipitate of perbromide, but in concentrated sulphuric acid one molecule of bromine is decolorised without the formation of perbromide. This enables the estimation of *apo*scopolamine when in admixture with scopolamine.

Scopoline contains two oxygen atoms, the one in an hydroxyl group, the other is fixed as an ether-like linking. Scopoline combines with concentrated sulphuric acid to form an ester acid, but chloroscopoline may be heated with this acid to about 100° without change.

Scopolamine hydrobromide has $[\alpha]_D^{18} -26°$; the commercial product reacts very faintly acid, but it is neutral to methyl-red after purification.

Atropropinesulphuric acid crystallises in lustrous, colourless prisms, m. p. 238—239°.

Scopolaminesulphuric acid crystallises in slender, stellar aggregates of matted needles, m. p. 244° (decomp.).

Homatropinesulphuric acid crystallises in rhombic platelets, m. p. 240°.

apo*Scopolamine* crystallises in long needles from ether or in well-formed prisms from light petroleum, m. p. 97°. The *nitrate* forms nacreous platelets, m. p. 157°; the *aurichloride* separates in feathery clusters of needles or well-formed thin prisms, m. p. 183—184°; the *picrate* consists of slender prisms, m. p. 217°, whilst the *methiodide* crystallises in short, stunted, lustrous prisms, m. p. 238° (decomp.).

[With E. P. Hedley].—*Scopolyl chloride* crystallises from ether in long prisms, b. p. 102—103°/8 mm. The *platinichloride* forms stunted prisms, m. p. 229—230° (decomp.). E. F. A.

Preparation of Quinine Esters of Aromatic Amino-acids. Vereinigte Chininfabriken Zimmer & Co. (D.R.-P. 244741).—The quinine esters of aromatic amino-acids have not previously been prepared.

p-*Nitrobenzoylquinine*, tasteless, yellow needles, m. p. 154°, obtained from quinine and *p*-nitrobenzoyl chloride, when reduced with stannous chloride furnishes p-*aminobenzoylquinine*, colourless crystals, m. p. 170°. o-*Nitrobenzoylquinine* forms tasteless needles, m. p. 164·5—166·5°, and o-*aminobenzoylquinine*, octahedra, m. p. 135—137·5°; the *hydrochloride*, $C_{20}H_{23}O_2N_2\cdot CO\cdot C_6H_4\cdot NH_2,2HCl$, is a yellow, tasteless powder with anæsthetic properties. F. M. G. M.

Buphane disticha (Hæmanthus toxicarius). Louis Lewin (*Arch. exp. Path. Pharm.*, 1912, 68, 333—340).—Hæmanthine, the alkaloid obtained from this plant, is a narcotic. Its action on the heart resembles that of the tropeines; it is also an emetic.

W. D. H.

Trimethyldi*apo*harmine, a New Base Obtained by the Application of Hofmann's Reaction to *apo*Harmine. Victor Hasenfratz (*Compt. rend.*, 1912, **154**, 1520—1523. Compare this vol., i, 209, 383).—Hofmann's reaction when applied to *apo*harmine does not bring about its degradation, but on the contrary a complex base containing four atoms of nitrogen is formed.

Methyl*apo*harmine unites with methyl iodide, forming *methyl*

apo*harmine methiodide*, $C_8H_7N_2Me_2I$, which is not acted on by potassium hydroxide. With moist silver oxide, it yields the corresponding *methohydroxide*, $C_8H_7N_2Me_2{\cdot}OH$, which in solution has a very alkaline reaction and an intense blue fluorescence. On evaporating the solution under reduced pressure and distilling the residue, *trimethyldi*apo*harmine*, $C_{16}H_{18}Me_3N_4$, is obtained as a yellow oil, which finally solidifies and crystallises from alcohol or ether in colourless plates, m. p. 74·5°. It yields a *platinichloride*, $C_{19}H_{22}N_4,H_2PtCl_6$, and a *dimethiodide*, which is soluble in water and alcohol. W. G.

Replacement of the Halogen in Chloro-α-methylmorphimethine by Hydroxyl. ROBERT PSCHORR and F. DICKHÄUSER (*Ber.*, 1912, **45**, 1570—1579).—When the halogen in chlorocodeine is replaced by hydroxyl, the three isomerides of codeine are obtained, instead of codeine itself. Somewhat analogous behaviour has now been observed with chloro-α-methylmorphimethine, which when heated with dilute acids forms γ-, ε-, or δ-methylmorphimethine respectively, with the elimination of hydrogen chloride. The changes causing the isomerism evidently take place in both instances in the reduced benzene nucleus of the phenanthrene residue.

When chloro-α-methylmorphimethine is hydrolysed above 100°, a further product is a dihydrate of a methylmorphimethine,

$$C_{19}H_{23}O_3N,2H_2O,$$

in which one molecule of water is a part of the molecular structure. This hydrate is obtained from ε-methylmorphimethine on heating a solution of the acetate, and it can be converted into ε-methylmorphimethine by heating it in a vacuum at 80°. The *dihydrate* crystallises in lustrous needles, m. p. about 100°; the *monohydrate* is hygroscopic, m. p. 112° (decomp.).

When heated with acetic anhydride and precipitated by potassium iodide, the *hydriodide* of the *monoacetylated hydrate* is obtained in prisms, decomp. 170°; the *base* forms slender needles, m. p. 130—131°.

E. F. A.

Methylation of the Alcoholic Hydroxyl in the Codeines II. Methylation of *iso*- and ψ-Codeine. ROBERT PSCHORR and F. DICKHÄUSER (*Ber.*, 1912, **45**, 1567—1570. Compare Abstr., 1911, i, 908).—The method of methylation of codeine previously described (*loc. cit.*), that is, treatment of the aqueous alkaline solution or suspension with excess of methyl sulphate or methyl iodide, is extended to *iso*- and ψ-codeine. The product from ψ-codeine is identical with the quaternary salt of the codeine methyl ether obtained by Knorr and Roth (Abstr., 1911, i, 1014) by the action of sodium methoxide on α-chlorocodide, proving that in this reaction of Knorr and Roth conversion into the ψ-series has taken place.

*Methyl*iso*codeine methiodide* crystallises in lustrous platelets, which sinter at 196°, m. p. 199—200°. On boiling with sodium hydroxide, *γ-methylmorphimethine methyl ether* is obtained, crystallising from light petroleum in lustrous, four-cornered platelets, m. p. 41°. The *hydroiodide* formed long, lustrous needles, which sinter at 189°, m. p. 192—193°, $[\alpha]_D^{22}+20{\cdot}31°$.

When the hydrochloride of γ-methylmorphimethine methyl ether is

heated with sodium acetate in a sealed tube at 150°, *δ-methylmorphimethine methyl ether* is obtained in narrow platelets, m. p. 71—72°; the *hydriodide* forms broad needles, m. p. 212°. β-Methylmorphimethine methyl ether, previously described as an oil, has been obtained from light petroleum in colourless prisms, m. p. 82°, $[\alpha]_D^{17}$ +432°. The hydriodide consists of prisms, decomp. 243°.

ψ-Codeinemethyl ether methiodide crystallises in large, stunted prisms, m. p. 270—271° (decomp.).

ε-Methylmorphimethine methyl ether crystallises in large prisms, m. p. 75°, $[\alpha]_D^{18}$ −92·48°; the hydriodide consists of platelets, which sinter at 200°, decomp. 207°. E. F. A.

Preparation of Methylenedicotarnine. Martin Freund (D.R.-P. 245622).—*Methylenedinarcotine*, $CH_2(C_{22}H_{22}O_7N)_2$, m. p. 215—216°, is prepared by the action of formaldehyde on narcotine; when treated with oxidising agents, it furnishes *methylenedicotarnine*,

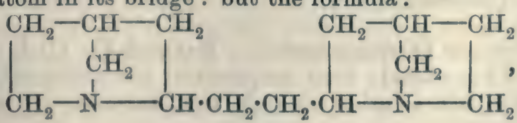
$$CH_2(C_{12}H_{14}O_4N)_2,$$

m. p. 132° (decomp.); its salts are yellow; the *hydriodide* has m. p. 235° (decomp.), and the *hydrobromide* decomposes at about 240°. These compounds are of therapeutic value. F. M. G. M.

Oxidation of Sparteine with Potassium Permanganate. A. Germain (*Gazzetta*, 1912, **42**, i, 447—450; *Boll. Chim. Farm.*, 1912, **51**, 111—113).—Bamberger (Abstr., 1887 162) and Ahrens (Abstr., 1887, 1056) having obtained contradictory results in studying the oxidation of sparteine with permanganate, the author has investigated the reaction in sulphuric and in phosphoric acid solution.

In the former case, no change takes place in the cold for a longer or shorter time according to the concentration of the acid, but if this is lowered by addition of increasing quantities of an alkali, the stability is diminished more and more, until, in a neutral medium, oxidation is almost instantaneous. No matter what the concentration of the acid, oxidation proceeds with great rapidity as soon as it begins, and is accompanied by vigorous evolution of carbon dioxide. The principal product of the reaction is oxalic acid, small proportions of ammonia and of a base giving a picrate, m. p. 168—169°, being also formed; in no case was a precipitate formed with copper acetate.

In presence of phosphoric acid the oxidation commences immediately, but proceeds very slowly, and is complete only after about a week. The main product is succinic acid, so that the presence of a four-carbon atom chain must be assumed in the sparteine molecule, and Moureu and Valeur's formula (Abstr., 1905, i, 716) requires modification. Numerous investigations have shown that the nuclei of sparteine are piperidinic in character, and hence incapable of undergoing oxidation to a four-carbon atom chain, which must hence be assumed to form the connecting link between the two nuclei. The conclusion is therefore drawn that at least one of the nuclei has only one carbon atom in its bridge: but the formula:



,

is less by CH_2 than that of sparteine, which is to be regarded as a higher homologue. Confirmation of this result is afforded by the behaviour of coniine, which gives *n*-butyric acid on oxidation.

T. H. P.

Preparation of Readily Soluble Double Compounds from Aminoacylphenetidines, Caffeine, and Mineral Acids. CHEMISCHE WERKE VORM. HEINRICH BYK (D.R.-P. 244740. Compare this vol., i, 516).—The aminoacylphenetidines combine with caffeine to form readily soluble double salts analogous to those furnished by dialkylaminodimethylpyrazolones; the reaction is carried out with equimolecular proportions of the components (or their salts) in either aqueous or alcoholic solution.

The patent describes a *compound* obtained from caffeine and aminoaceto-*p*-phenetidide ($OEt\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH_2$) in dilute hydrochloric acid solution.

F. M. G. M.

Action of Ammonia on Derivatives of Piperidone, Pyridone, and Hydropyrone. N. TSONEFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 662—664).—The interaction of ethyl or methyl diphenylpiperidonedicarboxylate with a small quantity of alcoholic ammonia in a sealed tube at 100° yields the *diamide*,

$$CO<\begin{matrix}CH(CO\cdot NH_2)\cdot CHPh\\ CH(CO\cdot NH_2)\cdot CHPh\end{matrix}>NH,$$

m. p. 245—247°. With the esters of pyridonedicarboxylic acid, no such reaction occurs with ammonia.

The compound obtained by heating ethyl 1 : 5-diphenylhydropyrone-2 : 4-dicarboxylate with alcoholic ammonia in a sealed tube, melts at 125—126°, and has the constitution $NH{:}C<\begin{matrix}CH(CO_2Et)\cdot CHPh\\ CH(CO_2Et)\cdot CHPh\end{matrix}>O$ or

$$NH_2\cdot C<\begin{matrix}CH(CO_2Et)\cdot CHPh\\ C(CO_2Et)\text{—}CHPh\end{matrix}>O.$$

T. H. P.

4 : 4-Dimethylpiperidine. GUSTAV KOMPPA (*Ann. Acad. Sci. Fennicae*, 1911, *A*, **3**, 6 pp. Compare *Chem. Zeit.*, 1906, **30**, 1184).—$\beta\beta$-Dimethylglutarimide (needles, m. p. 146°), obtained from the corresponding acid anhydride by the action of ammonia, is reducible by sodium and alcohol to 4 : 4-*dimethylpiperidine*,

$$CMe_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>NH,$$

b. p. 145—146°; *hydrochloride*, needles, m. p. 220—221°; *platinichloride*, prismatic crystals; *aurichloride*, m. p. 168° (decomp.). The base reacts with phenylthiocarbimide, giving 4 : 4-*dimethylpiperidylphenylthiocarbamide*, needles, m. p. 136°.

D. F. T.

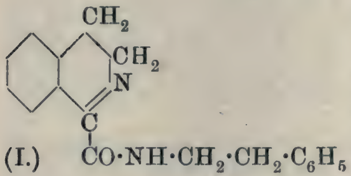
[**Hæmopyrrole.**] HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1912, **78**, 420).—Polemical. A reply to Marchlewski (this vol., i, 399).

E. F. A.

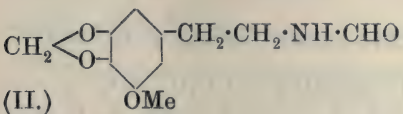
Preparation of Dibromoisatin. KALLE & Co. (D.R.-P. 245042). Dibromoisatin has already been prepared by the action of bromine on isatin in acetic acid solution at high temperatures. It is now found

that the reaction goes smoothly and at a lower temperature in sulphuric acid solution. If sulphuric acid (66 Bé) is employed, only monobromoisatin is formed, whereas dibromoisatin, an orange-yellow powder, m. p. 248—250, is obtained in quantitative yield when isatin (14·7 parts) in 150 parts of sulphuric acid (60° Bé) is treated with bromine (32 parts), left at the ordinary temperature during twenty-four hours, then slowly heated to 40°, and subsequently at 80°. F. M. G. M.

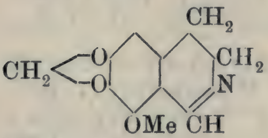
Preparation of Dihydro*iso*quinoline Derivatives. HERMANN DECKER (D.R.-P. 245095. Compare Trans., 1910, **97**, 1212; Abstr., 1911, i, 906). — *Oxalylbisphenylethylamine*, glistening needles, m. p. 186°, is prepared by fusing together phenylethylamine (2 mols.) and oxalic acid (1 mol.); when treated with phosphoric oxide in toluene solution it furnishes


(I.)

the *base* (formula I) [*dihydro*iso*quinoline-2-carboxyphenylethylamide*]; the *picrate*, $C_{24}H_{21}O_8N_5$, canary-green needles, has m. p. 167—168°, the *hydrochloride*, colourless needles, m. p. 191—193°; when heated under pressure during four hours with 15% hydrochloric acid at 180°, it is decomposed into dihydro*iso*quinoline and phenylethylamine hydrochlorides with evolution of carbon dioxide.


(II.)

Formyl-3-methoxy-4:5-methylenedioxyphenylethylamine (formula II) has m. p. 105—106°, and when treated with phosphoryl chloride furnishes 8-*methoxy*-6:7-*methylenedioxy*-3:4-*dihydro*iso*quinoline* (formula III), a dark oily base, which finally solidifies, but has no well defined m. p. (the *picrate* has m. p. 182—184°), and on methylation yields cotarnine hydriodide.


(III.)

F. M. G. M.

Condensation Products of 2:4-Dimethylquinoline with Aldehydes. ROSARIO SPALLINO and A. CUCCHIARONI (*Gazzetta*, 1912, **42**, i, 517—525).—In view of the readiness with which a methyl group in the 2-position of the pyridine or quinoline nucleus reacts with aldehydes, the authors have investigated 2:4-dimethylquinoline in this direction in order to ascertain if the 4-methyl group can also be made to react. With all the aldehydes employed, however, it was found that the 4-methyl group did not react, even when an excess of the aldehyde was employed and the reaction was carried out in presence of zinc chloride. This condensing agent has, indeed, a harmful effect, since, in addition to causing resinification, it forms compounds with the quinoline derivatives, from which the latter are separated only with difficulty.

With *chloral*, 2:4-dimethylquinoline forms the condensation product

[4-*methyl-2-tri-γ-chloropropenylquinoline*], $C_9H_5NMe\cdot CH{:}CH\cdot CCl_3$, which forms nacreous, rectangular plates, m. p. 124°, exhibits normal cryoscopic behaviour in benzene, and combines with bromine, giving 4-*methyl-2-tri-γ-chloro-αβ-dibromopropylquinoline*,

$$C_9H_5NMe\cdot CHBr\cdot CHBr\cdot CCl_3,$$

m. p. 155°. The unsaturated condensation product is basic in character, its *hydrochloride* having m. p. 152°; it is readily hydrolysed by alkali, giving 4-*methylquinoline-2-acrylic acid*, $C_9H_5NMe\cdot CH{:}CH\cdot CO_2H$, which begins to decompose at 190° and melts at about 210°, and readily reduces permanganate and absorbs bromine.

If the reaction between 2 : 4-dimethylquinoline and chloral is arrested before its completion, the result is an aldol *condensation product*, $C_9H_5NMe\cdot CH_2\cdot CH(OH)\cdot CCl_3$, which forms white, prismatic needles, m. p. 67°, and gives the unsaturated product, m. p. 124°, when heated.

With *benzaldehyde*, 2 : 4-dimethylquinoline yields the condensation product [2-*styryl-4-methylquinoline*], $C_9H_5NMe\cdot CH{:}CHPh$, which forms thick, lemon-yellow needles, m. p. 122—123°, gives a *hydrochloride*, m. p. 259° (decomp.), and a *dibromide*, m. p. 162°, decolorises permanganate solution, and yields benzoic and 4-methylquinoline-2-carboxylic acids on oxidation.

The following condensation products [substituted 2-styryl-4-methylquinolines] were also examined :

With o-*nitrobenzaldehyde*, $C_9H_5NMe\cdot CH{:}CH\cdot C_6H_4\cdot NO_2$, m. p. 140—141°; *hydrochloride* decomposes at 200°; *bromide*, m. p. 505° (decomp.).

With m-*nitrobenzaldehyde*, m. p. 184°; the hydrochloride and bromide decompose on heating.

With *vanillin*, $C_9H_5NMe\cdot CH{:}CH\cdot C_6H_3(OH)\cdot OMe$, golden-yellow scales, m. p. 217°; the *hydrochloride* decomposes at 256°. T. H. P.

Preparation of Aryl Esters of 2-Phenylquinoline-4-carboxylic Acid. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 244788).—The methyl and ethyl esters of 2-phenylquinoline-4-carboxylic acid have already found therapeutic employment, and the following additional compounds have now been prepared; the *phenyl* ester, m. p. 132°, and the *β-naphthyl* ester, yellow crystals, m. p. 130°.

F. M. G. M.

Dibromophenyl*iso*oxazolone and Derivatives. ANDRÉ MEYER (*Compt. rend.*, 1912, 154, 1511—1514).—4 : 4-*Dibromo-3-phenyliso-oxazolone*, $O{<}\begin{matrix}CO\cdot CBr_2\\ \quad\ \ |\\ N{=}CPh\end{matrix}$, is obtained as colourless crystals, m. p. 76—77°, by the action of bromine on phenyl*iso*oxazolone in acetic acid solution. It condenses with phenylhydrazine, giving a phenylhydrazone, which is identical with Claisen's benzeneazophenyl*iso*oxazolone (compare Abstr., 1891, 468). With *as*-phenylmethylhydrazine it forms the *hydrazone*, $C_{16}H_{13}O_2N_3$, m. p. 148°, and with *as*-phenylbenzylhydrazine the *hydrazone*, $C_{22}H_{17}O_2N_3$, m. p. 126—127°. With *as*-benzoylphenylhydrazine no hydrazone is formed, but the product is benzeneazophenyl*iso*oxazolone. It gives a *semicarbazone*, $C_{10}H_8O_3N_4$, which crystallises in pale yellow

needles, m. p. 230—232°, and an oxime which is identical with oximinophenyl*iso*oxazolone.

Amines cause the elimination of bromine, heterocyclic amines giving rise to rubazonic acids. Aminoantipyrine condenses with dibromophenyl*iso*oxazolone, giving 1-phenyl-2 : 3-dimethylpyrazoloneimino-3′-phenyl*iso*oxazolone (compare Abstr., 1911, i, 687).

With indoxyl, 3-phenyl*iso*oxazolone-2-indole is obtained (compare Wahl, Abstr., 1909, i, 261). W. G.

Diphenylethylene Leuco-bases and Colouring Matters; Some Alkylaminoethylenic Derivatives. PAUL LEMOULT (*Compt. rend.*, 1912, **154**, 1622—1625. Compare Abstr., 1911, i, 399).—*p*-Alkylaminophenyl ketones, for example, Michler's ketone, when treated with a Grignard reagent produce ethylenic substances (Freund and Mayer, Abstr., 1906, i, 384; Busignies, Abstr., 1909, i, 736). The reaction is now extended by the application of Grignard reagents from other alkyl halides; the reaction product generally consists of a mixture of a grey powder insoluble in alcohol, with the expected ethylenic compound.

Magnesium *n*-propyl iodide with Michler's ketone gives *di*-p-*dimethylamino-αα-diphenyl-Δ^α-butylene*, $CH_2Me\cdot CH{:}C(C_6H_4\cdot NMe_2)_2$, colourless needles, m. p. 47·5°.

Magnesium *iso*propyl iodide in a similar manner gives the isomeric *di*-p-*dimethylamino-αα-diphenyl-β-methyl-Δ^α-propylene*,

$$CMe_2{:}C(C_6H_4\cdot NMe_2)_2,$$

compact crystals with a green tinge, m. p. 89°.

Magnesium *n*-butyl iodide gives di-*p*-dimethylamino-*αα*-diphenyl-Δ^α-amylene, $CH_2Me\cdot CH_2\cdot CH{:}C(C_6H_4\cdot NMe_2)_2$, colourless needles, m. p. 50·5°.

Magnesium *iso*butyl iodide gives *di*-p-*dimethylamino-αα-diphenyl-γ-methyl-Δ^α-butylene*, $CHMe_2\cdot CH{:}C(C_6H_4\cdot NMe_2)_2$, which refused to crystallise; a reddish-brown, crystalline *substance* which contained iodine was obtained as a by-product.

Magnesium *sec.*-butyl iodide gives *di*-p-*dimethylamino-αα-diphenyl-β-methyl-Δ^α-butylene*, $CMeEt{:}C(C_6H_4\cdot NMe_2)_2$, compact, pale yellow crystals, m. p. 79°.

The above products give solutions in acetic acid, which gradually attain an intense blue colour; they also give colour reactions with nitrous acid and with manganese dioxide. D. F. T.

Hexahydrogenated Malachite-green; an Example of Two Different Leuco-bases which Yield the Same Dye. PAUL LEMOULT (*Compt. rend.*, 1912, **154**, 1354—1356. Compare Abstr., 1911, i, 399).—The author has reduced *cyclo*hexenyltetramethyldiaminodiphenylmethane to *cyclo*hexyltetramethyldiaminodiphenylmethane (Wahl and Meyer, Abstr., 1910, i, 134) by means of hydriodic acid and red phosphorus. The latter compound yields no coloration when oxidised by lead peroxide in acid solution. Chloranil in benzene solution oxidises it to malachite-green, the six additional hydrogen atoms of the *cyclo*hexane group being removed. The conclusion is drawn that the existence of a dye containing the *cyclo*hexyl group is improbable. H. W.

Reaction between Carboxylic Acids and Benzenesulphonamide at High Temperatures. CHARLES A. ROUILLER (*Amer. Chem. J.*, 1912, 47, 475—497).—Nakaseko (this vol., i, 452) has suggested that the "infusible diamide" obtained by the action of heat on *m*-sulphamidobenzoic acid is *m*-sulphobenzenylamidine,

$$SO_3H\cdot C_6H_4\cdot C(:NH)\cdot NH_2.$$

This structure has now been confirmed by the observation that the "infusible diamide" yielded by *p*-sulphamidobenzoic acid (Remsen and Muckenfuss, Abstr., 1896, i, 481) can be obtained by heating *p*-sulphobenzoic acid with benzenesulphonamide. It has also been shown that carbamidobenzenesulphonic acid is probably formed as an intermediate compound in the production of the "infusible diamide," since benzenylamidine benzenesulphonate can be obtained from benzamide and benzenesulphonamide.

When a mixture of benzoic acid (1 mol.) and benzenesulphonamide (2 mols.) is heated at 225°, benzenesulphonic acid and benzenylamidine benzenesulphonate are produced, together with small quantities of benzonitrile, cyaphenin, and benzoic acid, the main reaction being represented as follows: $C_6H_5\cdot CO_2H + 2C_6H_5\cdot SO_2\cdot NH_2 = C_6H_5\cdot C(:NH)\cdot NH_2,C_6H_5\cdot SO_3H + C_6H_5\cdot SO_3H$, or in two stages, thus: $C_6H_5\cdot CO_2H + C_6H_5\cdot SO_2\cdot NH_2 = C_6H_5\cdot CO\cdot NH_2 + C_6H_5\cdot SO_3H$ and $C_6H_5\cdot CO\cdot NH_2 + C_6H_5\cdot SO_2\cdot NH_2 = C_6H_5\cdot C(:NH)\cdot NH_2,C_6H_5\cdot SO_3H$. Benzenylamidine benzenesulphonate, m. p. 173°, first prepared by Robinson (*Diss.*, 1906), behaves towards alkali hydroxides, magnesium hydroxide, and acids in an analogous manner to the "infusible diamide" from *p*-sulphamidobenzoic acid. In order to confirm the view that benzamide is formed as an intermediate product, benzamide (1 mol.) and benzenesulphonamide (1 mol.) were heated together at 220°; it was found that benzenylamidine benzenesulphonate could be obtained in this way, but only in presence of benzenesulphonic acid. Benzenylamidine *p*-toluenesulphonate (Robinson, *loc. cit.*) melts at 193°.

Ethenylamidine benzenesulphonate, m. p. 136°, obtained by heating a mixture of acetic acid (1 mol.) and benzenesulphonamide (2 mols.) at 220°, forms long, transparent needles. This method of preparing amidines was applied to various aliphatic and aromatic acids; in several cases, amidine benzenesulphonates were produced, whilst in others negative results were obtained.

m- and p-*Nitrobenzenylamidine benzenesulphonates* have m. p. 198—200° and 250° respectively. m-*Bromobenzenylamidine benzenesulphonate* has m. p. 156—158°, and *phenylethenylamidine benzenesulphonate*, m. p. 182—183°. When phthalic acid is heated with benzenesulphonamide, a nearly quantitative yield of phthalimide is produced. *iso*Phthalic and terephthalic acids, however, yield the corresponding nitriles as the main products, together with small quantities of the cyanobenzoic acids; terephthalic acid gives also a small quantity of p-*cyanobenzenylamidine benzenesulphonate*,

$$CN\cdot C_6H_4\cdot C(:NH)\cdot NH_2,C_6H_5\cdot SO_3H,$$

m. p. 215—218°. E. G.

Urocanic Acid. ANDREW HUNTER (*J. Biol. Chem.*, 1912, 11, 537—546).—The details of analysis given prove that urocanic acid is β-iminazole-4(5)-acrylic acid. W. D. H.

Hydantoins. XI. New Method of Synthesising *N*-Alkyl Derivatives of α-Amino-acids. Methyltyrosine. TREAT B. JOHNSON and BEN H. NICOLET (*Amer. Chem. J.*, 1912, 47, 459—475).—*N*-Methyltyrosine (α-methylamino-β-*p*-hydroxyphenylpropionic acid) has been prepared by Friedmann and Gutmann (Abstr., 1910, i, 741). It is now shown that this compound can be readily obtained from 4-anisylidenehydantoin (Wheeler and Hoffman, Abstr., 1911, i, 499). By the action of methyl iodide on 4-anisylidenehydantoin, 4-anisylidene-1 : 3-dimethylhydantoin is produced, which, on reduction with hydriodic acid, yields 1 : 3-dimethyltyrosinehydantoin, and this when hydrolysed with barium hydroxide furnishes the barium salt of methyltyrosine. The amount of methyltyrosine obtained after removing the barium corresponds with 32% of the theoretical.

The syntheses can be modified by reducing the 4-anisylidene-1 : 3-dimethylhydantoin to 4-*p*-methoxybenzyl-1 : 3-dimethylhydantoin by means of tin and hydrochloric acid and converting this, by hydrolysis with barium hydroxide, into α-methylamino-β-*p*-methoxyphenylpropionic acid (Friedmann and Gutmann, *loc. cit.*), which when heated with hydriodic acid gives a yield of methyltyrosine amounting to 65% of the theoretical.

Methyltyrosine has no definite m. p., but decomposes between 265° and 320°, according to the rate of heating.

4-*Anisylidene*-1 : 3-*dimethylhydantoin*,

$$OMe\cdot C_6H_4\cdot CH{:}C<\begin{matrix}CO-NMe\\ NMe\cdot CO\end{matrix},$$

m. p. 84—85°, forms yellow prisms. 4-*Anisylidene*-1-*methylhydantoin*, $OMe\cdot C_6H_4\cdot CH{:}C<\begin{matrix}CO-NMe\\ NH\cdot CO\end{matrix}$, m. p. 218°, obtained as a by-product in the preparation of the dimethyl compound, crystallises in needles. 4-p-*Hydroxybenzyl*-1 : 3-*dimethylhydantoin* (1 : 3-*dimethyltyrosinehydantoin*), $OH\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}CO-NMe\\ NMe\cdot CO\end{matrix}$, m. p. 149—150°, forms rhombohedric crystals. 4-p-*Hydroxybenzyl*-1-*methylhydantoin* (1-*methyltyrosinehydantoin*), $OH\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}CO-NMe\\ NH\cdot CO\end{matrix}$, m. p. 200°, obtained by reducing 4-anisylidene-1-methylhydantoin with hydriodic acid and amorphous phosphorus, crystallises in short, colourless prisms.

4-p-*Methoxybenzyl*-1 : 3-*dimethylhydantoin*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}CO-NMe\\ NMe\cdot CO\end{matrix},$$

was obtained as a light brown oil; it can also be prepared by treating 4-*p*-methoxybenzylhydantoin with methyl iodide in presence of alkali hydroxide. α-Methylamino-β-p-methoxyphenylpropionic acid crystallises in colourless, prismatic needles, and decomposes between 220° and 255°, according to the rate of heating.

1-*Phenyl*-4-p-*methoxybenzyl*-3-*methyl*-2-*thiohydantoin*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}CO-NPh\\ NMe\cdot CS\end{matrix},$$

m. p. 105°, prepared by the action of phenylthiocarbimide on

α-methylamino-β-p-methoxyphenylpropionic acid, crystallises in colourless prisms.

4-p-Methoxybenzylhydantoin (Wheeler, Hoffman, and Johnson, Abstr., 1911, i, 923) can be prepared in a yield of 78% of the theoretical by reducing 4-anisylidenehydantoin with tin and alcoholic hydrogen chloride.

By the action of iodine on methyltyrosine in presence of potassium hydroxide, *α-methylamino-β-3 : 5-di-iodo-4-hydroxyphenylpropionic acid* (*methyliodogorgoic acid*), $OH\cdot C_6H_2I_2\cdot CH_2\cdot CH(NHMe)\cdot CO_2H$, is obtained in 76% yield; it forms nearly colourless crystals and decomposes at about 205°. E. G.

Some Homologues of Auramine and Crystal-violet. BERTHOLD RASSOW and OTTO REUTER (*J. pr. Chem.*, 1912, [ii], 85, 497—513).—The interaction of auramine-G (dimethyldiaminodi-o-tolyliminomethane) and methyl sulphate in alcoholic solution in the presence of magnesium oxide yields *trimethyldiaminodi-*o*-tolyliminomethane methyl sulphate*, $NHMe\cdot C_7H_6\cdot C(NH_2)\colon C_7H_6\colon NMe_2\cdot SO_4Me$, which crystallises in small, reddish-brown, basalt-like prisms, m. p. 243—244°, and when boiled with hydrochloric acid is converted into *trimethyldiaminodi-*o*-tolyl ketone*, $NHMe\cdot C_7H_6\cdot CO\cdot C_7H_6\cdot NMe_2$. This forms a light yellow, crystalline powder, m. p. 128—129°, and yields a *dihydrochloride*, crystallising in small, lustrous, silvery leaflets, m. p. 216°; the *picrate* forms light orange crystals, m. p. 171°.

*Tetramethyldiaminodi-*o*-tolyl ketone*, $CO(C_7H_6\cdot NMe_2)_2$, prepared by methylating dimethyldiaminodi-o-tolyl ketone (Gnehm and Wright, Abstr., 1902, i, 295) with methyl sulphate and magnesium oxide in benzene solution, crystallises in clusters of long, flat, pale yellow needles, m. p. 85·5°, b. p. 240—250°/12 mm.; the *dihydrochloride* forms slender, white needles, m. p. 204—206° (decomp.); the *platinichloride*, $C_{19}H_{24}ON_2,H_2PtCl_6$, crystallises with alcohol (1 mol.) and decomposes at 240°; the *oxalate*, m. p. 171—172°, and *picrate*, small yellow needles, m. p. 192°, are also described.

The *methyl sulphate* is obtained as a viscid, reddish-brown oil by carrying out the methylation in the absence of magnesium oxide.

*Tetramethyldiaminodi-*o*-tolylcarbinol*, $OH\cdot CH(C_7H_6\cdot NMe_2)_2$, prepared by reducing the preceding ketone with sodium amalgam and alcohol, forms a white powder, m. p. 76°; the *picrate* becomes green at 140°, and has m. p. 145°.

When heated with ammonium chloride and zinc chloride, tetramethyldiaminodi-o-tolyl ketone yields an auramine *dye*,

$$NMe_2\cdot C_7H_6\cdot C(NH_2)\colon C_7H_6\colon NMe_2Cl,$$

as a yellow powder which chars at 250°.

*Tetramethyltriaminophenyldi-*o*-tolylcarbinol hydrochloride*,

$$NHMe\cdot C_7H_6\cdot C(C_6H_4\cdot NMe_2)\colon C_7H_6\colon NHMeCl,$$

prepared by condensing dimethyldiaminodi-o-tolyl ketone and dimethylaniline with phosphorus trichloride, forms small, green, lustrous crystals, and dyes cotton, mordanted with tannin, reddish-violet; the corresponding *carbinol* is precipitated in brownish-red flocks on the addition of aqueous sodium hydroxide to the hydrochloride.

*Pentamethyltriaminophenyldi-*o*-tolylcarbinol hydrochloride*,

$$C_{26}H_{32}N_3Cl,$$

obtained from trimethyldiaminodi-*o*-tolyl ketone and dimethylaniline in a similar manner, forms a deep blue, hygroscopic, crystalline powder, having a metallic lustre; the reddish-brown *carbinol*, $C_{26}H_{33}ON_3$, could not be obtained crystalline.

The condensation of tetramethyldiaminodi-*o*-tolyl ketone and dimethylaniline by means of phosphoryl chloride yields *hexamethyltriaminophenyldi-o-tolylcarbinol hydrochloride*,

$$NMe_2{\cdot}C_7H_6{\cdot}C(C_6H_4{\cdot}NMe_2){:}C_7H_6{:}NMe_2Cl,$$

which forms a dark violet, crystalline powder of a feeble metallic lustre; the corresponding *carbinol* forms white crystals, m. p. 115—116°.

The preceding penta- and hexa-methyl derivatives dye cotton, mordanted with tannin, bluish-violet and blue respectively. F. B.

Tri-indylmethane Dyes. III. ALEXANDER ELLINGER and CLAUDE FLAMAND (*Zeitsch. physiol. Chem.*, 1912, **78**, 365—372. Compare König, Abstr., 1911, i, 808).—According to König, the formation of the dye, $C_{19}H_{16}N_2,HCl$, from methylindole-aldehyde takes place without oxidation. The authors formulate the change as involving three molecules of methylindole-aldehyde and an atom of oxygen, giving the dye, $C_{28}H_{23}N_3,HCl$. König's formula is supported by analyses of the salts, but these alone are insufficient to decide between the two formulæ. Both molecular-weight determinations and the estimation of the amount of formic acid formed confirm the formula $C_{28}H_{23}N_3$.

Indyldichloromethylindylmethane, prepared from indylaldehyde and chloromethylindole, forms colourless plates, which become yellowish-rose on the surface on exposure to light, and have m. p. 263°. E. F. A.

Nitrosodimethyluracilnitriloxide. RUDOLF BEYTHIEN (*Annalen*, 1912, **389**, 214—232).—The green substance obtained by Behrend and Hufschmidt by the nitration of 1 : 3 : 4-trimethyluracil (Abstr., 1906, i, 311) is shown to be 5-nitroso-1 : 3-dimethyluracil-4-nitriloxide, $NMe{<}{\begin{matrix}CO{\cdot}C(NO)\\CO{-}NMe\end{matrix}}{>}C{\cdot}C{<}{\begin{matrix}O\\|\\N\end{matrix}}$, the presence of the pyrimidine nucleus being proved by the formation of nitrodimethyluracilcarboxylic acid by its further nitration. It has m. p. 170—171° (decomp.), crystallises from alcohol in green needles, from benzene in green prisms, and best from glacial acetic acid in pale green, rhombic plates, and its unimolecular structure is proved by the cryoscopic method in the last solvent. It is converted by 36% hydrochloric acid on the water-bath into *dimethylvioluric acid*, $C_6H_7O_4N_3,H_2O$, m. p. 123° (decomp.), or 140—141° when anhydrous, which produces a violet coloration with alkalis and is converted into dimethyldilituric acid by nitric and sulphuric acids.

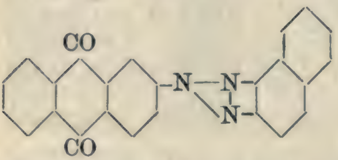
The reduction of nitrosodimethyluracilnitriloxide by tin and hydrochloric acid at the ordinary temperature yields *azodimethyluracilcarboxyamide*,

$$CO{<}{\begin{matrix}NMe{-}{-}{-}{-}CO\\NMe{\cdot}C(CO{\cdot}NH_2)\end{matrix}}{>}C{\cdot}N{:}N{\cdot}C{<}{\begin{matrix}CO{-}{-}{-}{-}NMe\\C(CO{\cdot}NH_2){\cdot}NMe\end{matrix}}{>}CO,$$

m. p. 227°, orange-yellow needles (which is reduced to aminodimethyluracilcarboxylic acid by further treatment with tin and hydrochloric

acid on the water-bath), and 5-amino-1 : 3-dimethyluracil-4-carboxylic acid, $C_7H_9O_4N_3,H_2O$, m. p. 215—224° (decomp.), which has strongly acidic properties, contrary to the statement of Behrend and Hufschmidt (*loc. cit.*). When aminodimethyluracilcarboxylic acid is boiled with 5% sodium hydroxide, ammonia is given off, and after acidifying the solution, carbon dioxide is obtained, together with a *substance*, $C_6H_8O_3N_2$, m. p. 224—225°, which has acidic properties, does not give a blue coloration with ferric chloride, and is regarded as 1 : 3-dimethyliminoazole-2-one-4-carboxylic acid, $CO_2H\cdot C{<}\begin{array}{l}CH{-}NMe\\ NMe\cdot CO\end{array}$, since it does exhibit the murexide reaction and is oxidised to dimethylparabanic acid by chromic acid. C. S.

Preparation of Anthraquinone Derivatives Containing the ψ-Azimino-Ring. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 245973).—When the aminoazo-derivatives obtained from diazotised β-aminoanthraquinones and β-naphthylamines are submitted to the action of oxidising agents they yield new compounds containing the ψ-azimino-ring, which find employment as yellow pigments.



aβ-Naphthylene-ψ-azimino-β-anthraquinonyl (annexed formula) crystallises from nitrobenzene, has m. p. 300° (approx.), and is prepared by dissolving the product obtained from diazotised β-aminoanthraquinone coupled with β-naphthylamine in nitrobenzene and treating it with sodium dichromate in acetic acid.

The preparation of the following analogous *compounds* are described in the original: from diazotised β-aminoanthraquinone with β-naphthylamine-3 : 6-disulphonic acid; with β-naphthylamine-6-sulphonic acid, and with 2 : 6-naphthylenediamine. From diazotised 2 : 6-diaminoanthraquinone with β-naphthylamine, and with β-naphthylamine-6-sulphonic acid. These compounds are all yellow or brownish-yellow powders. F. M. G. M.

Preparation of Aminoanthraquinonyltriazoles. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 245191).—When the anthraquinonyltriazoles which are obtained by the oxidation of *o*-aminoazoanthraquinone derivatives are nitrated and subsequently reduced, they yield compounds of tinctorial value. β-Anthraquinonyl-1 : 2-naphthylenetriazole (37 parts) dissolved in concentrated sulphuric acid (400 parts) was slowly treated with potassium nitrate (10·1 parts), and the *nitro*-compound isolated in the form of a yellow powder; this when reduced with sodium sulphide furnished *amino-β-anthraquinonyl-1 : 2-naphthylenetriazole*, a brown powder which is soluble in concentrated sulphuric acid with an orange coloration. When a larger quantity of potassium nitrate is employed, more highly nitrated products are obtained. F. M. G. M.

Purines. 2 : 8-Dioxy-6 : 9-dimethylpurine and 2 : 8-Dioxy-1-methylpurine. CARL O. JOHNS (*J. Biol. Chem.*, 1912, 11, 393—400).—6-Chloro-2-ethylthiol-4-methylpyrimidine was heated in a

sealed tube with methylamine; the 6-*methylamino-2-ethylthiol-4-methylpyrimidine* so obtained, flat prisms, m. p. 87°, was converted into 6-*methylamino-4-methyl-2-pyrimidone*, m. p. 290°, which when nitrated gave 5-*nitro-6-methylamino-4-methyl-2-pyrimidone*, stout prisms, m. p. 250°; this was reduced by ferrous hydroxide to 5-amino-6-methylamino-4-methyl-2-pyrimidone, forming anhydrous needles, m. p. 270°. By heating this with carbamide, 2:8-*dioxy*-6:9-*dimethylpurine* was obtained; it crystallises ($2H_2O$) in needles, m. p. 320°.

2:8-*Dioxy*-1-*methylpurine* was obtained by heating 5:6-diamino-3-methyl-2-pyrimidone with carbamide as small, anhydrous plates, not melting at 320°. W. D. H.

Uric Acid Glycol. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1912, 45, 1677—1682).—Alluranic acid was obtained by Mulder by the evaporation of an aqueous solution of alloxan and carbimide (this Journ., 1874, 49). On the analogy of the formation of substituted uric acid glycols (compare Abstr., 1910, i, 526, and following abstract), this acid should be the glycol of uric acid itself. It has now been prepared by allowing the mixed solutions to evaporate in a desiccator over lime, in flat prisms with half a molecule of water. When warmed with glacial acetic acid the anhydrous acid is obtained, m. p. 203—205°, and when heated with hydriodic acid it is reduced to hydantoin, which confirms its constitution.

Attempts have been made to convert the glycol into the isomeric 5-*hydroxyhydantoylcarbamide*, $C_5H_6O_5N_4$, but this only takes place in warm water; the new compound is very soluble in water, but practically insoluble in organic media, and decomposes at 204—206°. When treated with hydrochloric acid in ethyl acetate, ammonium chloride is precipitated, and a syrupy residue, the caffolide, is formed. Hydrolysis by means of hydrochloric or nitric acid leads to the elimination of carbamide, and the residue of the molecule can be characterised by reduction to hydantoin. J. C. W.

The Reduction of the Uric Acid Glycols to Hydantoins. Some Salts of the Uric Acid Glycols. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1912, 45, 1666—1677).—It was hoped that the reduction of uric acid glycols (compare Abstr., 1910, i, 526) would furnish some uric acids which are difficult to obtain. This could not be realised, as many reducing agents are without effect, but hydriodic acid readily reduces these substances to hydantoins, the alloxan nucleus being opened or eliminated.

7:9-Dimethyluric acid glycol gives the new 1:3-dimethylhydantoin; the formation of 3-methyl-(or ethyl)-hydantoin from the glycols produced by condensing alloxan with methyl-(or ethyl)-carbamide decides for position 9 for the alkyl group; and the production of 1-methylhydantoin from 3:7-dimethyluric acid glycol, on the one hand, and from caffeine, on the other, shows that the carbon atom 5 of the uric acid system becomes the methylene carbon of the hydantoin system. Only one glycol, 1:3-dimethyluric acid glycol, behaved differently, amalic acid being produced. This lesser stability of the

glyoxalone nucleus is no doubt due to the fact that neither imino-group is alkylated (compare Biltz, Abstr., 1909, i, 740; 1910, i, 523).

E. Fischer's method for the preparation of 1-methylhydantoin from *apo*caffeine (Abstr., 1883, i, 354) has been shortened by the direct reduction of the latter to hydrocaffuric acid, which is then hydrolysed by baryta, the best results being obtained by this means.

Methylparabanic acid, when reduced by fuming hydriodic acid, is converted into a mixture of 1- and 3-methylhydantoins, which are very difficult to separate (compare Weitzner, Abstr., 1908, i, 841). The reduction of 7 : 9-dimethyluric acid glycol also requires the concentrated agent, as weaker acid leads partly to dimethylparabanic acid which can scarcely be separated.

1 : 3-*Dimethylhydantoin*, $C_5H_8O_2N_2$, crystallises from ether in pointed leaflets, m. p. 44—45°, and distils as a colourless, mobile liquid at 262°. Having ascertained its properties, it was found possible to prepare it by the reduction of 1 : 3 : 6-trimethylallantoin, from which Fischer could only separate the accompanying methylcarbamide (*loc. cit.*), and by the energetic reduction of dimethylparabanic acid. The latter process gives a yield of 67%, and as the acid is easily obtained by the oxidation of caffeine, it is the best to adopt. This hydantoin is very susceptible towards alkalis, baryta converting it into the barium salt of 1 : 3-dimethylhydantoic acid, and for this reason it could not be obtained from deoxy*allo*caffuric acid (Abstr., 1910, i, 523).

When warmed with alcoholic ammonia, 3 : 7-dimethyl-, 7 : 9-dimethyl-, 9-methyl-, and unsubstituted uric acid glycols form unstable *mono-ammonium* salts, which give up their ammonia when kept. In the case of the 1 : 3-dimethyluric acid glycol, however, the glyoxalone ring is opened. When mixed with silver nitrate and then made alkaline with ammonia, *di-silver* salts are precipitated, the imide hydrogens being replaced; positions 1 and 9 are most readily filled. 7 : 9-Dimethyluric acid glycol gives no silver salt. When warmed with methyl iodide the silver is replaced, but degradation to caffolides also takes place, highly methylated uric acid glycols being unstable.

J. C. W.

Dilatometric Investigations on the Precipitation of Proteins. GINO GALEOTTI (*Zeitsch. physiol. Chem.*, 1912, 78, 421—434).—Coagulation produced by heat and by enzymes causes no change of volume in proteins. There is, however, an increase in volume seen when egg-albumin is precipitated by protein-precipitants. This is maximal when ammonium sulphate is used (a reversible reaction), medium in the case of salts of the heavy metals, and minimal in the case of potassium ferrocyanide, phosphotungstic acid, and tannin.

W. D. H.

General Chemistry of the Proteins. IV. Protein Scission and Soap-protein Compounds PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1912, 41, 165—173).—In following out the course of digestion of proteins by a stalagmometric method it was observed that the surface tension of liquids increased when the solution of proteins was digested by means of acids, whereas it

remained unchanged when the proteins were digested with enzymes. This was found to hold with all the proteins investigated, with the exception of gelatin, and the fact indicates that certain products are formed in digestion by ferments (possibly adsorption compounds) which undergo further change when treated with acids. It was also observed that blood diminishes the capacity of soaps for lowering the surface tension, the corpuscles acting, in this respect, about ten times as powerfully as the serum. This also indicates the formation of protein-soap adsorption compounds. A similar action was not found in the case of other substances, such as amyl acetate and tributyrin, which lower the surface tension of water. S. B. S.

Pseudo-globulin. H. C. HASLAM (*Proc. physiol. Soc.*, 1912, xiii—xiv; *J. Physiol.*, 44).—Globulin and ψ-globulin are to be regarded as distinct chemical individuals; they can be separated by fractional precipitation with salts; ψ-globulin contains no phosphorus, globulin does. W. D. H.

The Laws of Combination of Hæmoglobin with Oxygen and Carbon Monoxide. C. G. DOUGLAS, JOHN S. HALDANE, and J. B. S. HALDANE (*J. Physiol.*, 1912, 44, 275—304).—When hæmoglobin (free or in corpuscles) is saturated with a mixture of oxygen and carbon monoxide, the ratio of oxy- and carboxy-hæmoglobin is proportional to the tensions of the two gases, and is not altered by the presence of carbon dioxide or reduced hæmoglobin, by slight changes in reaction, or by dilution, but is appreciably altered by temperature and by light, and varies in the hæmoglobin of different individuals and species. In human blood, the dissociation curves agree closely with Barcroft's, but in mouse's blood there are great differences. When the pressures of oxygen and carbon monoxide are so low that reduced hæmoglobin is present, the proportions of oxy-, carboxy-, and reduced hæmoglobin can be calculated if the dissociation curves of the two former are known; in consequence of the form of these curves, it follows that a small proportion of oxygen may increase the formation of carboxyhæmoglobin. W. D. H.

The Cataphoresis of Oxyhæmoglobin. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1912, 41, 102—110. Compare Abstr., 1910, ii, 48).—The authors confirm their previous determinations of the isoelectric point of oxyhæmoglobin and show that it is not affected by the presence of small quantities of impurities in the form of either colloids or salts. In carrying out the experiments with salt mixtures of higher concentration (phosphates), it was found that the isoelectric zone was broadened. The isoelectric point was also determined in mixtures of cacodylic acid and its sodium salt.

S. B. S.

Sturine. ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1912, 78, 402—413).—Sturine contains a repetition of the grouping $-NH\cdot CHR\cdot CO-$; it breaks down into arginine, histidine, lysine, alanine, and leucine, or an isomeride. Of the total nitrogen, between

67·4 and 66·7% is present as arginine, 10·1 to 9% as histidine, 7·5 to 5·5% as lysine, the numbers representing the maximal and minimal amounts possible.

The basicity of sturine corresponds with 24 atoms of nitrogen per 100 atoms of nitrogen present, whilst the arginine in it is equivalent only to 17 atoms; histidine and lysine must, therefore, be concerned in the basicity.

All three hydrogen atoms in the iminazole (histidine) nucleus of sturine are free and not concerned in the peptide formation. On treatment with nitrous acid, a *deaminosturine* is obtained, which contains the same percentage of arginine and histidine, no lysine, and more monoamino-acid than sturine.

With nitric acid, a nitrosturine is obtained, which forms nitroarginine on hydrolysis.

On treatment with $N/2$-sodium hydroxide at 37° for some days and subsequent hydrolysis, inactive amino-acids are obtained. The change, as Dakin has explained (Abstr., 1910, i, 590), is due to the enolisation of the carbonyl group, and its occurrence proves that the acid carboxyl groups were bound in the molecule as suggested; it has become ···NH·CH:C(OH)·NH·CR':C(OH)··· after treatment.

On partial hydrolysis of sturine, protones are obtained containing varying proportions of arginine, histidine, and lysine. E. F. A.

Preparation of Secretin. HENRY H. DALE and PATRICK P. LAIDLAW (*Proc. physiol. Soc.*, 1912, xi—xii; *J. Physiol.*, 44).—Secretin can be prepared by precipitating it in the form of a mercury compound; the mercury is removed by hydrogen sulphide, and a very active preparation is thus obtained when required for use. It is relatively free from the depressor substance. The composition of secretin itself is still unknown. W. D. H.

A Synthetic Action of Emulsin. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 154, 1375—1378; *J. Pharm. Chim.*, 1912, [vii], 5, 569—573).—With the object of demonstrating the synthetic action of enzymes, the authors have submitted an alcoholic solution of dextrose and saligenin to the action of emulsin. The course of the action was followed by means of the polarimeter, the final readings of which corresponded with that deduced for the quantity of salicin expected. Attempts to isolate salicin from the reaction product were unsuccesful. In its place a non-crystalline substance, $[\alpha]_D - 30·02°$, was obtained, which scarcely reduced Fehling's solution, and was rapidly hydrolysed by emulsin. It is possibly β-ethylglucoside (Koenigs and Knorr, Abstr., 1901, i, 369). H. W.

The Supposed Reversibility of the Hydrolysis of Salicin by Enzymes. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1912, 154, 1646—1648. Compare Bourquelot and Bridel, this vol., i, 522, and preceding abstract; Visser, Abstr., 1905, ii, 577; Tammann, Abstr., 1892, 899).—The authors view with suspicion the experi-

mental proofs adduced as to the reversible nature of the hydrolysis of salicin by emulsin.

In a careful series of experiments in which the amount of hydrolysis was determined by the reducing effect of the dextrose formed (Bertrand, Abstr., 1907, ii, 136), they find that salicin in 1% and 3% solutions at various temperatures is completely hydrolysed in a comparatively short time. Even if a little salicin is introduced into a solution of equimolecular quantities of the products of hydrolysis (dextrose and saligenin), the addition of emulsin causes hydrolysis of the salicin. D. F. T.

Action of Emulsin on Gentiopicrin in Solution in Neutral Organic Liquids. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, **154**, 1259—1261; *J. Pharm. Chim.*, 1912, [vii], **5**, 534—549).—It has been shown previously that the decomposition of gentiopicrin or salicin by emulsin must take place by direct contact, since hydrolysis goes on in alcohol in which emulsin is insoluble (Abstr., 1911, i, 1053; this vol., i, 522). It is now shown that gentiopicrin is not hydrolysed by emulsin suspended in dry acetone, but that hydrolysis takes place slowly with acetone containing 10% of water, and more rapidly when larger proportions of water are added, being complete in thirty-seven days when acetone containing 40% of water is used. Similarly, no hydrolysis takes place in dry ethyl acetate, but complete hydrolysis occurs in ten days when 20% of the ester saturated with water is added, and more rapidly when larger proportions of the wet ester are employed. Hydrolysis also takes place when solutions made by macerating emulsin in acetone containing at least 50% of water are used, but not with liquids prepared by macerating emulsin in wet ethyl acetate. T. A. H.

Enzyme Action. II. Hydrolytic Action of Some Amino-acids and Polypeptides on Certain Esters. K. GEORGE FALK and JOHN M. NELSON (*J. Amer. Chem. Soc.*, 1912, **34**, 828—845. Compare this vol., i, 522).—It is suggested that the hydrolytic action of lipase is due to an active protein, which is readily hydrolysed in aqueous solution to form lipolytically inactive substances. In order to test this hypothesis, the hydrolytic action of various amino-acids and polypeptides on methyl acetate, ethyl butyrate, and olive oil has been studied.

The results indicate a peculiar selective character in the action of the amino-acids and polypeptides; thus glycine exerts its greatest hydrolytic action on ethyl butyrate, and phenylalanine on methyl acetate. This selective action is suggestive of that of lipases from different sources with different esters, and it seems probable that many of these selective actions of the lipases may be reproduced with amino-acids and polypeptides of varying structure or in presence of other substances.

There is no evidence, however, that the hydrolytic action of lipase is due to amino-acids or polypeptides, but the specific groups in these substances which show this activity may be also present in the proteins, and it is therefore considered probable that a study of the

decomposition products, such as amino-acids, from preparations showing lipolytic activity, or of the more complex polypeptides or other substances synthesised from them, may throw light on the substances capable of causing lipolytic action. E. G.

Enzyme Action. Urease: a Selective Enzyme. Henry Edward Armstrong and Edward Horton (*Proc. Roy. Soc.*, 1912, *B*, **85**, 109—127).—The enzyme in these experiments was prepared from Soja beans (compare Takeuchi, Abstr., 1909, ii, 925), and was found to hydrolyse carbamide with ease. The action of the enzyme on the substituted carbamides (methylcarbamide, *s*-dimethylcarbamide, *as*-dimethylcarbamide, ethylcarbamide, *s*-diethylcarbamide, and on biuret) was tested, and the results indicate that it is capable of acting only on carbamide itself. It is, therefore, specific in effect, and must correspond closely in structure with carbamide.

The rate of change is dependent to a certain extent on the concentration of the solution of carbamide employed, since the amount of action in $M/5$-solutions is equal to that in M-solution, and more than twice as much as in $5M$-solutions.

The effects of the products of change were investigated, and it was found that the addition of ammonia, equal to one-tenth of the amount producible from the carbamide added, limited the conversion to a decided extent. On the other hand, ammonium carbonate had a much less effect, whilst carbon dioxide increased the activity of the enzyme. Similar stimulation was obtained by the use of glycine. It appeared conceivable that the ammonia limited the change either by its action as an alkali or by promoting the destruction of the enzyme, but this was shown by experiment not to be the case.

The effect of various salts and non-electrolytes on hydrolysis was tested, and it was found that whilst ammonium chloride and dextrose have a slight accelerating action, potassium and sodium chlorides retard the change.

The process of conversion is regarded as being one of hydration and hydrolysis, the hydrolyte being the hydrated form of carbamide, $C(OH)_2(NH_2)_2$. This compound can give rise to cyanic acid if deprived of ammonia and hydrone; if hydrolysed, it can give rise to orthocarbonic acid and ammonia.

The function of urease would seem to be to determine the change in the latter direction; in other words, to condition the direct hydrolysis of carbamide and thereby prevent its reversion into cyanate. The repressing and stimulating action exercised by certain salts and non-electrolytes can be accounted for by assuming the enzyme to be a feebly acidic substance, and that in order to effect change it must unite with the feebly basic carbamide. A more basic substance, such as ammonia, would interfere with such union and consequently retard change. Carbon dioxide by fixing the ammonia would facilitate the action of the enzyme by leaving it free to act as hydrolyst.

H. B. H.

The Mode of Action of Phosphatese. III. Hans Euler (*Biochem. Zeitsch.*, 1912, 41, 215—223. Compare Abstr., 1911, i, 1057; this vol. i, 403).—In view of the controversy between Iwanoff

and Harden and Young as to whether the synthesis of organic compounds of phosphorus from phosphates by yeast can take place without fermentation, the view held by Iwanoff as opposed to that held by Harden and Young, the author calls attention to two facts: (1) Under the influence of extract of dried yeast, a synthesis of dextrose-phosphoric acid esters can take place, provided that the dextrose is first submitted to fermentation by yeast; (2) that such a synthesis can take place without evolution of carbon dioxide. The author draws attention to the fact that the various yeasts differ considerably with regard to the amount of synthesising enzyme (phosphatese) which can be extracted by maceration. He also replies to criticisms on his work by Lebedeff. S. B. S.

Preparation of Nitrohydroxyarylarsinic Acids. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 245536).—1-*Chloro-2-nitrophenyl-4-arsinic acid*, colourless leaflets decomposing suddenly without melting, when heated, can be prepared by nitrating 1-chlorophenyl-4-arsinic acid (Abstr., 1908, i, 591); when gently warmed with about five parts of a solution of potassium hydroxide (36° Bé), the chlorine atom is replaced by hydroxyl, yielding the therapeutically valuable 2-nitrophenol-4-arsinic acid (Abstr., 1911, i, 1056).

1-*Chloro-o-tolyl-4-arsinic acid*, needles, m. p. 180°, can be obtained from *o*-toluidine-4-arsinic acid (*loc. cit.*) by decomposing its diazonium chloride in the presence of cuprous chloride; when nitrated, it furnishes 1-*chloro-6-nitro-o-tolyl-4-arsinic acid*, yellow needles, m. p. 310°, which by the action of sodium hydroxide is converted into nitro-*o*-cresol-4-arsinic acid. F. M. G. M.

Preparation of Neutral Aqueous Soluble Derivatives of 3:3′-Diamino-4:4′-dihydroxyarsenobenzene. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 245756).—When 3:3′-diamino-4:4′-dihydroxyarsenobenzene hydrochloride (25 parts) dissolved in 250 c.c. of water is slowly treated with twenty-five grams of formaldehydesulphoxylate dissolved in 125 c.c. of water and after some hours 80 c.c. of a 10% solution of sodium carbonate added, a clear yellow solution is formed, which when treated with mineral acid furnishes a *compound* in the form of a reddish-yellow powder and containing one acidic sulphur group; the *sodium* salt can be precipitated by alcohol. If in the foregoing reaction the formaldehyde sulphoxylate is added to a suspension of the free base and the mixture gently warmed at 60—70°, a *compound* containing two acidic sulphur groups is formed; these compounds are insoluble in the ordinary organic solvents and in acids, but dissolve readily in alkali carbonates or ammonium hydroxide; and the solutions of their alkali salts have a neutral reaction. F. M. G. M.

Preparation of 5-Nitro-2-aminophenyl-1-arsinic Acid. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 243693. Compare Abstr., 1909, i, 980; 1910, i, 148).—5-Nitro-2-aminophenyl-1-arsinic acid is obtained in comparatively good yield by heating arsenic acid (20 parts) with *p*-nitroaniline (70 parts) at 210°, with removal of the evolved water by distillation (compare this vol., i, 61).

F. M. G. M.

Preparation of *p*-Amino-*m*-hydroxyarylarsinic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 244166. Compare Abstr., 1911, i, 1056).—When diazotised solutions of 3-nitro-4-aminoaryl-1-arsinic acids are treated with agents which combine with mineral acids (such as sodium acetate), the nitro-group is replaced by hydroxyl, yielding compounds which combine readily with β-naphthol, resorcinol, 8-amino-α-naphthol-5-sulphonic acid, and 1 : 8-dihydroxynaphthalene-4-sulphonic acid.

p-*Amino*-m-*hydroxyphenylarsinic acid*, a crystalline powder, is obtained by the cautious reduction at 30° of the foregoing hydroxyazo-β-naphthol derivative with sodium hyposulphite in alkaline solution. It is of therapeutic value; the *sodium* salt forms glistening scales and is readily soluble in water. F. M. G. M.

Preparation of Aminohydroxy-derivatives and Homologues of Arsenobenzenes. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 244789 and 244790. Compare Abstr., 1910, i, 803; 1911, i, 594, 1056; preceding abstract).—When 2-nitro-1-aminoaryl-4-arsinic acids are diazotised and treated with acid withdrawing agents (such as sodium acetate), the nitro-group is replaced by hydroxyl and the so-obtained hydroxydiazonium compounds combine readily with resorcinol, the naphthols, and the other azo-dye forming components; the *compound* from 2-nitro-1-aminophenyl-4-arsinic acid and β-naphthol forms glistening coppery crystals, and by energetic reduction furnishes 4 : 4′-*diamino*-3 : 3′-*dihydroxyarsenobenzene* as a yellow powder. The second patent describes the preparation of the foregoing base by reducing 1-amino-2-hydroxyphenyl-4-arsinic acid (*loc. cit.*) with sodium hyposulphite at 60—65°. F. M. G. M.

Preparation of Carboxylic Acid Esters Containing Mercury and the Products of their Hydrolysis. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 245571. Compare Trans., 1907, 91, 557).—When the esters of unsaturated cyclic carboxylic acids are treated with mercuric acetate in 98% alcohol, compounds are formed which readily undergo hydrolysis and furnish the corresponding acids containing mercury.

Mercuric acetate (30 parts) in 98% alcohol (20 parts) was slowly treated with ethyl chaulmoograte (25 parts) and left during twenty-four hours, the alcohol was separated under diminished pressure, and the *product* extracted from the residue (by means of ether) as a colourless oil, containing 33—35% of mercury, which when hydrolysed with alcoholic potassium hydroxide furnished a mercury containing chaulmoogric acid. Ethyl Δ^1-*cyclo*hexenecarboxylate yielded a similar *compound*, which was obtained in crystalline form, and on hydrolysis furnished the *anhydride* of a carboxylic acid containing mercury.

F. M. G. M.

Organic Chemistry.

Remarks on the Nomenclature of Organic Chemistry. CONSTANTIN I. ISTRATI (*Bull. Soc. chim.*, 1912, [iv], **11**, 565—570).—An outline of the principles on which is based a new system of nomenclature, with regard to which a book is shortly to be published by the author. W. G.

Sodium Copper Thiosulphate and Acetylene Cupro-acetylide. KAHITIBHUSAN BHADURI (*Zeitsch. anorg. Chem.*, 1912, **76**, 419—421).—When acetylene is passed into a solution of sodium thiosulphate and copper acetate, a red precipitate is obtained, which dissolves in water, but may be washed with alcohol. It forms a brick-red powder, which burns like gunpowder when heated. It decomposes slowly at 33°, or in ten hours on the water-bath. The red solution is decolorised by acids; the colour is restored on adding alkali immediately, but not after a short time. Alkalis, except ammonia, precipitate a brown, explosive substance. The analysis of the red product agrees with the formula

$$5Na_2S_2O_3,5Cu_2S_2O_3,5Cu_2C_2,C_2H_2,10H_2O.$$

C. H. D.

Autoxidation of Trichloroethylene. ERNST ERDMANN (*J. pr. Chem.*, 1912, **86**, [ii], 111—112).—A reply to Staudinger (this vol., i, 330). F. B.

Synthesis of Compounds of the Nona- and Undeca-methylene Series. JULIUS VON BRAUN and E. DANZIGER (*Ber.*, 1912, **45**, 1970—1979).—When $\alpha\eta$-dibromoheptane is boiled with potassium cyanide in aqueous alcoholic solution the nitrile of azelaic acid, $CN\cdot[CH_2]_7\cdot CN$, is obtained as a colourless liquid, b. p. 183°/11 mm.; on reduction with sodium and alcohol, $\alpha\iota$-diaminononane is formed, yielding a dibenzoyl derivative, m. p. 121°. When this is warmed with phosphorus pentachloride and distilled in a vacuum, $\alpha\iota$-dichlorononane is obtained; this is a colourless liquid of pleasant odour, b. p. 138—139°/17 mm. The residue of the distillation contains the *chlorinated amide*, $Cl\cdot[CH_2]_9\cdot NHBz$, the crystals of which have m. p. 75°. On heating with hydrochloric acid, *chlorononylamine hydrochloride* is obtained as a syrup. The *platinichloride* is egg-yellow in colour; it blackens at 177°, decomp. 193—195°.

When chloromethyl ether is added slowly to a cooled mixture of $\alpha\eta$-dibromoheptane and magnesium, *$\alpha\iota$-dimethoxynonane* is obtained in good yield, together with other products; it has b. p. 114—115°/10 mm. When warmed with fuming hydrobromic acid at 100°, $\alpha\iota$-dibromononane is obtained, m. p. 154—155°/10 mm.

The dibromononane leads in a similar manner to *nonane-$\alpha\iota$-dicarboxylonitrile*, $CN\cdot[CH_2]_9\cdot CN$, a transparent, odourless liquid,

b. p. 195—198°/12 mm., which is converted into nonane-$\alpha\iota$-dicarboxylic acid, m. p. 109°, on hydrolysis identical with that described by Walker and Lumsden (Trans., 1901, 79, 1194).

On reduction of the nitrile, the *hydrochloride* of *ακ-diaminoundecane* is obtained in colourless crystals, m. p. 254—255°. The *platinichloride* is orange-yellow, blackens at 200°, decomp. 221°. The benzoyl derivative of the diamine has m. p. 112°.

αλ-Dichloroundecane is a transparent liquid, b. p. 156—158°/16 mm.

λ-Chloroundecylbenzamide has m. p. 64—66°.

αλ-Di-iodoundecane, obtained on heating the dichloro-derivative with sodium iodide, has b. p. 200—208°/15 mm. It reacts with sodium phenoxide readily to form *αλ-diphenoxyundecane*,

$$OPh\cdot[CH_2]_{11}\cdot OPh,$$

m. p. 52°.

Of the twelve homologous diphenyl ethers, those with an uneven number of carbon atoms have a lower melting point than those with an even number of carbon atoms.

αλ-Dimethoxyundecane has b. p. 128—135°/12 mm.; it is converted on heating with hydrogen bromide into *αλ-dibromoundecane*, b. p. 170—175°/15 mm.

When either dibromo- or di-iodo-undecane is condensed with potassium cyanide, the *nitrile* formed, b. p. 210—215°/16 mm., yields brassylic acid on hydrolysis. E. F. A.

Dehydration of Alcohols by means of Sulphonic Acids and the Influence of Phenols on this Reaction. HENRI WUYTS (*Bull. Soc. chim. Belg.*, 1912, 26, 304—309).—*tert.*-Butyl or *tert.*-amyl alcohols when heated with one-twentieth to one-sixtieth of their weight of toluene-4-sulphonic acid are converted into *iso*butylene or β-ethyl-Δ^{β}-butylene.

*iso*Propyl and *sec.*-butyl alcohols react less readily at their boiling point, but at a higher temperature, or when the proportion of the catalyst is increased to an equimolecular amount, they react quite smoothly and are converted into hydrocarbons.

sec.-Octyl alcohol is dehydrated at its boiling point; *cyclo*hexanol requires an elevated temperature; menthol is dehydrated by simple boiling with the sulphonic acid.

Toluene-4-sulphonic acid is decomposed when heated by itself at 155°, but in presence of sufficient alcohol (*cyclo*hexanol) no decomposition at this temperature was observed. The addition of a small quantity of phenol greatly facilitates the dehydration of the alcohol. The yield of hydrocarbon is, however, less than the theoretical quantity, and when a considerable proportion of phenol is added, homologues of phenol are obtained. Thus cyclo*hexylphenol* has m. p. 128°.

On heating phenol with β-methyl-Δ^{β}-butylene and toluene-4-sulphonic acid in a sealed tube at 100°, *tert.*-amylphenol is obtained. E. F. A.

Some Unsaturated Internal Ethers. J. W. LE HEUX (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 19—21).—Divinyl glycol (Griner, Abstr., 1893, i, 240) reacts with acetyl chloride to form a *chloroacetin*, b. p. 84—88°/18 mm., which is converted by concentrated,

aqueous sodium hydroxide into s-*divinyleth lene oxide*, $O<\begin{matrix}CH\cdot CH:CH_2\\ |\\ CH\cdot CH:CH_2\end{matrix}$, b. p. 108—109°, D^{15} 0·8834, n_D^{15} 1·44942. The oxide is a mobile liquid having the pungent odour of allyl compounds, resinifies in the presence of air and alkalis, regenerates the glycol by treatment with warm water, and absorbs hydrogen chloride. The ring is easily ruptured, since the oxide and allylamine yield a molecular additive *compound*, m. p. 37·5°.

Equal molecular quantities of hypochlorous acid and isoprene react at 0° to form a *compound*, C_5H_9OCl, b. p. 142—145°, which is converted by aqueous sodium hydroxide into a *substance*, b. p. 80—82°, the constitution of which is not yet decided. C. S.

Chemical Individuality in the Pinacone Series. MAURICE DELACRE (*Bull. Soc. chim. Belg.*, 1912, **26**, 227—236).—A résumé (compare Abstr., 1911, i, 32, 102, 347, 939). E. F. A.

Mechanism of the Hell-Volhard Reaction. OSSIAN ASCHAN (*Ber.*, 1912, **45**, 1913—1919).—The bromination of carboxylic acids at the α-carbon atom is rendered explicable if the following changes occur: $R\cdot CH_2\cdot CO_2\cdot H \longrightarrow CHR:C(OH)_2 \xrightarrow{Br_2} CHRBr\cdot CBr(OH)_2 \longrightarrow CHRBr\cdot CO_2H + HBr$. The theory can be tested by brominating an acid chloride; in this case an additive compound, $CHRBr\cdot CClBr\cdot OH$, would be formed, which should yield a mixture of brominated acid chloride and brominated acid bromide (the latter predominating) by loss of hydrogen bromide and hydrogen chloride.

[With ERIK FALCK.]—The theory has been tested and fully substantiated by the bromination of acetyl chloride, propionyl chloride, valeryl chloride, stearyl chloride, succinyl chloride, and camphoryl chloride; in all cases the acid evolved is a mixture of hydrogen chloride and hydrogen bromide, the former being in excess.

Chloroacetyl chloride is scarcely attacked by bromine even at 150°. C. S.

Hydrolysis of Esters of Substituted Aliphatic Acids. W. A. DRUSHEL (*Amer. J. Sci.*, 1912, [iv], **34**, 69—74).—The rates of hydrolysis of ethyl α- and β-monochloropropionates and of ethyl α- and β-monobromopropionates in *N*/10-hydrochloric and hydrobromic acid solution and in aqueous solution have been measured. Ethyl αα-dibromopropionate was found to be too sparingly soluble in water to permit similar determinations.

In the presence of *N*/10-hydrochloric or hydrobromic acid at temperatures not exceeding 35°, the ethyl esters of halogen substituted propionic acids decompose almost quantitatively according to the equation: $C_2H_4X\cdot CO_2Et + H_2O \longrightarrow C_2H_4X\cdot CO_2H + EtOH$. Below 35° the halogen substituted propionic acids decompose very slowly according to the equation $C_2H_4X\cdot CO_2H + H_2O \longrightarrow HX + OH\cdot C_2H_4\cdot CO_2H$. When decomposition takes place in this direction, the β-position of the halogen favours the reaction.

The velocity of hydrolysis of the ethyl esters of halogen substituted

propionic acids is much less than that of ethyl propionate in the presence of added catalysing acid, but much greater than when no catalyst is added. Esters with the halogen in the α-portion hydrolyse more rapidly than those with the halogen in the β-position when hydrolysis is carried out in the presence of added catalysing acid; the same is true when the hydrolysis is made in the absence of added catalysing acid if corrections are applied for the halogen acids set free by the hydrolysis of the halogen substituted propionic acids.

Ethyl β-chloropropionate, b. p. 162°, and *ethyl β-bromopropionate*, b. p. 85°/25 mm., were prepared by the action of the corresponding halogen on a solution of ethyl β-iodopropionate in chloroform.

Ethyl αα-dibromopropionate had b. p. 102—103°/38 mm. H. W.

Crystallisation of Sodium Palmitate. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1912, **26**, 193—198).—As the concentration of sodium palmitate solutions is increased, the temperature at which crystallisation begins becomes progressively higher. Separation of the salt takes place almost completely within a small range of temperature. In solutions of 0·05 to 0·025 N, which are limpid when warm, acicular crystals are formed at 47—45°, and there is a free separation at 43—42°. Solutions of 0·02N become cloudy at 45°, and deposit crystals at 42·5°, which separate freely at 40·5°. In more dilute solutions the liquids are opalescent at high temperatures and become iridescent at about 50°; very small crystals are formed between 40° and 36°. Still weaker solutions form granulations which separate as a crystalline deposit.

These results have been confirmed by determinations of the electrical conductivity of the solutions during cooling. The temperature at which crystallisation begins is indicated by a marked fall in the conductivity. The more dilute the solution, the lower is the temperature at which this fall is observed.

The curves connecting temperature and conductivity all show a marked confluence at the lower temperatures, indicating that the mother liquors have the same composition after crystallisation.

Similar curves drawn for sodium oleate show no gradual decrease.

The molecular conductivities of sodium palmitate are very small, and it is deduced that such soap solutions, particularly when not too dilute or warm, constitute colloidal media. E. F. A.

Glycerides of Fatty Acids. III. Heptadecoic Acid and its Triglyceride. ALOIS BÖMER and R. LIMPRICH (*Zeitsch. Nahr. Genussm.*, 1912, **23**, 641—653. Compare Abstr., 1907, i, 830; 1909, i, 284).—With regard to the question as to the occurrence of certain glycerides in various fats, the authors have prepared, for the purpose of comparison, specimens of heptadecoic acid and its glyceride. The method employed for the synthetic preparation of the acid was that described by Krafft (Abstr., 1880, 34). The pure acid crystallised from ether in the form of rhombic plates, m. p. 60·5°, b. p. 143·6° in a vacuum (absolute). One hundred c.c. of absolute alcohol dissolved 1·15 grams of the acid at 0°, and 3·48 grams at 15°. The zinc salt of the acid was practically insoluble in alcohol at 15°. The triglyceride of heptadecoic acid was also prepared, and found to have m. p. 62·7°.

One hundred c.c. of anhydrous ether dissolved 0·0288 gram of the glyceride at 0°, and 0·322 gram at 15°. Fine needle-shaped crystals of the glyceride were deposited from the ethereal solution. W. P. S.

Oil of Wallflower Seeds. HERMANN MATTHES and W. BOLTZE (*Arch. Pharm.*, 1912, **250**, 211—230).—The oil extracted by ether from wallflower seeds has a green colour changing to brown after long keeping, and contains 0·027% of ethereal oil (b. p. 120—125°/15 mm., D^{15} 0·9034, n_D^{20} 1·692, $[\alpha]_D$ −12·73°, iodine number 179·40). The residual cheiranthus oil has D^{15} 0·9240, n_D^{40} 1·4690, acid number 11·50, saponification number 180·30, ester number 168·80, iodine number 124·53, Hehner number 95·66, Reichert-Meissl number 0·33, and Polenske number 1·4. It is classified as a drying oil.

After hydrolysis with alcoholic potassium hydroxide and subsequent neutralisation with acetic acid, the oil is treated with aqueous lead acetate and benzene according to Farnsteiner's method for the separation of the fatty acids. The solid fatty acids obtained from hydrolysed oil of wallflower seeds consist of 5% of linolenic acid, 30% of linoleic acid, and 65% of a new unsaturated acid, *cheiranthic acid*, $C_{17}H_{33}\cdot CO_2H$, m. p. 30°, b. p. 240—245°/12 mm., n_D^{40} 1·4536, iodine number 71·16, which is optically inactive. Cheiranthic acid is converted by nitrous acid into an *isomeride*, m. p. 51—52°, n_D^{70} 1·4520, and is oxidised by alkaline potassium permanganate at 0°, and finally at the b. p., yielding a *dihydroxy-acid*, $C_{17}H_{33}(OH)_2\cdot CO_2H$, m. 118°, n_D^{60} 1·4570.

From the unsaponifiable constituents of the oil, a *phytosterol*, $C_{27}H_{46}O,H_2O$, has been isolated, which crystallises in colourless plates, and has m. p. 136°, $[\alpha]_D$ −31·78°, iodine number 77·14; it forms an *acetate*, m. p. 128—129°, *benzoate*, m. p. 142°, and *propionate*, m. p. 108°. C. S.

Direct Preparation of Organic Per-Acids. JOH. D'ANS and W. FREY (*Ber.*, 1912, **45**, 1845—1852).—The reaction between organic per-acids and water is a reversible one, and can be represented as $RCO\cdot OOH + H_2O \rightleftharpoons RCO_2H + H_2O_2$. The reverse reaction has been overlooked (Clover and Richmond, Abstr., 1903, i, 396), probably on account of its slowness, but it is now shown that the necessary catalytic effect can be supplied by sulphuric acid or nitric acid (or less well by hydrofluoric and phosphoric acids, and some salts). Equilibrium is then practically attained in twelve to sixteen hours, and even in two hours for formic acid. For equimolecular mixtures of the various acids with hydrogen peroxide, it is found that when equilibrium is attained, 61% of the formic acid, 68% of the acetic acid, and 68% of the propionic acid are converted into the corresponding per-acids. The reaction product can be distilled under reduced pressure, but it is difficult to obtain the pure per-acids in this way.

To obtain the free per-acids it is better to start with the acid anhydride, which reacts quantitatively with hydrogen peroxide according to the equation: $(RCO)_2O + H_2O_2 = R\cdot CO\cdot OOH + R\cdot CO\cdot OH$. The addition of sulphuric acid (preferably more than is necessary for the mere catalytic effect), together with another molecule of hydrogen

peroxide, gives a mixture which by distillation yields a highly concentrated solution, from which the per-acid can be separated by freezing-out and centrifugalising.

Per-acetic acid (compare D'Ans and Friederich, this vol., ii, 151) is obtained by adding cautiously (with cooling) a molecular quantity of hydrogen peroxide to one of acetic anhydride; the reaction may be violent. Sulphuric acid (1% calculated on $Ac_2O + 2H_2O_2$) and a second molecular quantity of hydrogen peroxide are then added, and the mixture left for twelve hours. On distillation at 10—20 mm. pressure (20—30°), a liquid is obtained .containing 78% of peracetic acid; if a larger quantity of sulphuric acid is used in the preparation, the percentage of per-acetic acid in the distillate may rise even above 90. The acid is a pungent and extremely explosive liquid, m. p. +0·1°; it explodes violently when warmed slowly to approximately 110°, near which temperature its b. p. lies; it keeps well in aqueous solution, but acids, alkalis, and salts hasten its hydrolysis to acetic acid and hydrogen peroxide; it is a powerful oxidising agent, and attacks the skin.

Perpropionic acid can be prepared in an analogous manner. Using 1% of sulphuric acid as catalyst, the distillate contains 78% of perpropionic acid, whilst with 17·56% of sulphuric acid the distillate contains 89·35% of per-acid. The properties of the acid are similar to those of per-acetic acid; it has m. p. −13·5°.

Butyric anhydride is miscible only with difficulty with hydrogen peroxide; the reaction, however, occurs readily, and a distillate can be obtained containing 91·2% of *perbutyric acid* (using 18·7% of sulphuric acid). The acid could not be obtained purer than 95·4%, when it had m. p. −10·5° Unlike the two previous acids, a dilute solution of perbutyric acid can be concentrated by keeping over anhydrous sodium sulphate.

Performic acid could only be obtained as a distillate containing 48% of the substance; it is not stable at room temperature, and forms carbon dioxide; also it is rapidly hydrolysed in aqueous solution.

An even simpler method for the preparation of organic per-acids consists in the action of hydrogen peroxide on the cooled mixture of anhydride with boric acid, according to the equation: $B(OAc)_3 + 3H_2O_2 = 3AcO_2H + B(OH)_3$. The per-acid is distilled off under reduced pressure; the yields are excellent, but the mixed acid anhydride is often difficult of preparation in a pure state.

Per-acetic acid is also formed in the action of hydrogen peroxide on keten, but it reacts immediately with more keten, giving as final product, diacetyl peroxide, the reactions being $CH_2{:}CO + H_2O_2 = CH_3{\cdot}CO{\cdot}OOH$; $CH_3{\cdot}CO{\cdot}OOH + CH_2{:}CO = (CH_3{\cdot}CO)_2O_2$. D. F. T.

Syntheses by means of Mixed Organo-metallic Derivatives of Zinc. α-Ethoxydialkylacetic Acids. Edmond E. Blaise and L. Picard (*Bull. Soc. chim.*, 1912, [iv], 11, 587—590. Compare this vol., i, 232, 410).—Ethyl dichloroglycollate condenses with mixed organo-zinc derivatives, giving ethyl ethoxydialkylacetates according to the equation:

$$OEt{\cdot}CCl_2{\cdot}CO_2Et + 2R{\cdot}Zn{\cdot}I = ZnI_2 + ZnCl_2 + OEt{\cdot}CR_2{\cdot}CO_2Et.$$

The condensation is effected at 0° in benzene solution, the ethyl dichloroglycollate being added gradually to the zinc alkyl iodide. The whole is left for two hours and is then treated with water, and the benzene solution separated, dried over anhydrous sodium sulphate, and the benzene driven off under reduced pressure.

Ethyl α-ethoxyisobutyrate, $OEt\cdot CMe_2\cdot CO_2Et$, so prepared is a colourless liquid, b. p. 54°/12·5 mm. On saponification with alcoholic potassium hydroxide, it yields the *acid*, $C_6H_{12}O_3$, b. p. 99°/14 mm., of which the *sodium*, *calcium*, and *copper* salts have been prepared. The ester reacts with magnesium aniline bromide, giving the *anilide*,

$$OEt\cdot CMe_2\cdot CO\cdot NHPh,$$

b. p. 190°/12 mm. The *α-naphthylamide*, m. p. 74°, is similarly prepared.

Ethyl α-ethoxy-α-ethylbutyrate, $OEt\cdot CEt_2\cdot CO_2Et$, as prepared by the general method, is a colourless liquid, b. p. 82°/14 mm., which, on saponification, gives the *acid*, $C_8H_{16}O_3$, b. p. 112·5°/13 mm. From it the *sodium*, *calcium*, and *copper* salts have been prepared. On boiling with aniline the acid does not yield an anilide, but an *aniline* salt, $C_8H_{16}O_3,NH_2Ph$, m. p. 101°. W. G.

Reduction of Hydroxymethylene Compounds. ARTHUR KÖTZ and ERNST SCHAEFFER (*Ber.*, 1912, **45**, 1952—1954).—Ethyl hydroxymethyleneacetoacetate, ethyl ethoxymethyleneacetoacetate, 2-hydroxymethylene*cyclo*hexanone, 4-hydroxymethylene-1-methyl*cyclo*hexan-3-one, 3-hydroxymethylene-1-methyl*cyclo*hexan-2-one, 2-hydroxymethylene-1-methyl-4-*iso*propyl*cyclo*hexan-3-one, and the chloride of hydroxymethylenecamphor have been reduced by hydrogen and palladium by the Paal-Skita method. In each case the hydroxymethylene group is reduced to the methyl group, and two molecular proportions of hydrogen are absorbed. C. S.

The Walden Rearrangement. BROR HOLMBERG (*Ber.*, 1912, **45**, 1713—1715).—The kinetics of the hydrolysis of *l*-bromosuccinic acid after exactly neutralising the acid with sodium hydroxide have been studied by measuring the change in rotation, the increase in acidity, and the bromine liberated. From the results the conclusion is drawn that the first change is the decomposition of the *l*-bromopropionic acid ion into bromine and propiolactonecarboxylic acid ions, the latter being dextrorotatory. The lactone is only slowly hydrolysed to malic acid; but as the latter is formed, it acts as a catalyst to accelerate this change. The malic acid acts also to retard the formation of the lactone from unchanged bromosuccinic acid.

The Walden change is represented: *l*-bromosuccinic acid $\longrightarrow$ *d*-malic lactone $\longrightarrow$ *d*-malic acid. E. F. A.

Experiments in the C_5 Series. 1. Preparation of Ether Lactones and Butyleneoxidecarboxylic Acid Esters. 2. A New Case of Alteration of Configuration (Walden Rearrangement) in Inactive Compounds with Several Asymmetric Carbon Atoms. HERMANN LEUCHS, MICHELE GINA, and JOSEPH F. BREWSTER (*Ber.*, 1912, **45**, 1960—1969. Compare Abstr., 1909, i, 361).—By the action of sodium ethoxide or sodium methoxide

on δ-chloro-γ-valerolactone, δ-ethoxy- and δ-methoxy-γ-valerolactones, $OR\cdot CH_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ O\text{---}CO\end{matrix}$, are obtained. In addition, isomeric substances of much lower boiling point and a strong ethereal odour are formed. They are butylene oxide derivatives, produced by the opening of the ring to $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO_2Me$, and subsequent elimination of hydrogen chloride to

$$\begin{matrix}CH_2\\ O\text{---}\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot CO_2Me.$$

By the action of dilute hydrogen chloride, the butylene oxide is readily reconverted into the chlorovalerolactone.

Traube and Lehmann (Abstr., 1901, i, 501) have shown that on chlorination of ethyl δ-chloro-γ-valerolactone-α-carboxylate a solid and an oily chloro-derivative are obtained. These were regarded as isomerides, which is now proved by analysis. They have been converted into γ-hydroxyproline through the αδ-dichloro-γ-valerolactones, with the result, however, that in both cases a mixture of α- and β-hydroxyprolines was obtained having the two isomerides in the proportion 3 : 2. By the substitution, a partial Walden rearrangement takes place, the system $\begin{pmatrix}d\text{-}d\\ l\text{-}l\end{pmatrix}$ becoming $\begin{pmatrix}d\text{-}l\\ l\text{-}d\end{pmatrix}$ and $\begin{pmatrix}d\text{-}d\\ l\text{-}l\end{pmatrix}$. This is analogous to the rearrangement in the case of dibromo- and *iso*dibromosuccinic acid when boiled with water.

δ-Methoxy-γ-valerolactone has b. p. 120—125°/12 mm. ; the corresponding δ-hydroxy-derivative has b. p. 122—123°/12 mm., D^{19} 1·113 ; it has only a faint odour.

Methyl αβ-butyleneoxide-δ-carboxylate is a mobile liquid, b. p. 83—85°/14 mm., D^{19} 1·069, and has an ethereal, melon-like odour.

δ-Ethoxy-γ-valerolactone has b. p. 123—124°/14 mm.

Ethyl αβ-butyleneoxide-δ-carboxylate has b. p. 92—94°/18 mm., 194—196°/760 mm., and resembles the methyl isomeride.

Amyl αβ-butyleneoxide-δ-carboxylate has b. p. 120—121°/10 mm., D^{19} 1·02. The odour is not strong ; when treated with hydrochloric acid, the odour of amyl alcohol is at once perceived.

αδ-Dichloro-γ-valerolactone is a thick, colourless oil, b. p. 159—161° (corr.), D^{19} 1·422 E. F. A.

Turkey Red Oil: New Derivatives of Ricinoleic Acid. M. Tschilikin (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 515—526).—Although, under some conditions, the action of sulphuric acid on ricinoleic acid (compare Grün, Abstr., 1907, i, 111) results in considerable diminution in the extent of unsaturation, the author finds that no such diminution is produced by the action of dry hydrogen chloride on ricinoleic and oleic acids.

In presence of formaldehyde, however, which is capable of reacting in the form $CH_2(OH)_2$ and of forming ethers, esters, and mixed ethereal-ester compounds, different results are obtained, the formaldehyde condensing with the hydroxyl of the acid. Thus the passage of dry hydrogen chloride through a mixture of ricinoleic acid, formaldehyde, and alcohol yields *ethyl methylenedioxydistearate*,

$$\begin{array}{l} CH_3\cdot[CH_2]_5\cdot\dot{C}H\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2Et \\ \qquad\qquad\quad \begin{matrix} O \\ O \end{matrix}\!\!>\!CH_2 \\ CH_3\cdot[CH_2]_5\cdot\dot{C}H\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2Et \end{array},$$

a saponification number 164·86 and an acid number zero. The free acid could not be isolated, its liberation being followed by condensation of the carboxyl group of one stearic acid residue with the CH(OH) group of the other, with loss of water. Under other conditions it was found possible to avoid the destruction of the double linking, the *dimethyl* ester,

$$\begin{array}{l} CH_3\cdot[CH_2]_5\cdot\dot{C}H\cdot CH_2\cdot CH\colon CH\cdot[CH_2]_7\cdot CO_2Me \\ \qquad\qquad\quad \begin{matrix} O \\ O \end{matrix}\!\!>\!CH_2 \\ CH_3\cdot[CH_2]_5\cdot\dot{C}H\cdot CH_2\cdot CH\colon CH\cdot[CH_2]_7\cdot CO_2Me \end{array},$$

with a saponification number 184·24—184·85, being obtained.

T. H. P.

Citrophosphate Solutions. ANTONIO QUARTAROLI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 478—479).—A reply to Pratolongo's criticisms (this vol., i, 412) on the author's conclusions (this vol., i, 238).

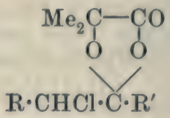
T. H. P.

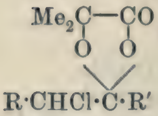
A New Observation with Angeli's Aldehyde Reaction. OSKAR BAUDISCH and J. H. COERT (*Ber.*, 1912, 45, 1775—1779).—The reaction between potassium hyponitrite and formaldehyde takes place with the intermediate formation of nitrosomethyl alcohol, $NO\cdot CH_2\cdot OH$, as witnessed by the momentary formation of a bluish-green coloration. The same should happen in Angeli's aldehyde reaction, and to make this visible the Angeli salt is dissolved in a little water, methyl acetate in large excess added, and the whole well shaken. The aqueous formaldehyde solution is now added; the methyl acetate becomes a deep bluish-green, the colour persisting for twenty-five seconds (compare also Steinkopf and Jürgens, Abstr., 1911, i, 530). E. F. A.

Action of Potassium Cyanide on Formaldehyde. KARL POLSTORFF and HERMANN MEYER (*Ber.*, 1912, 45, 1905—1912).—When 25% aqueous potassium cyanide and about 18% formaldehyde are mixed slowly at 0° and the mixture kept at the ordinary temperature for twenty-four hours, ammonia is evolved, and the solution contains glycollic acid, iminodiacetic acid, and nitrilotriacetic acid. The formation of these acetic acids is due to the initial production of glycollonitrile, the presence of which is proved by treating the alkaline solution, a few minutes after mixing, with methyl sulphate, whereby methoxyacetonitrile (Gauthier, Abstr., 1909, i, 353) is obtained. During the twenty-four hours' keeping, the glycollonitrile is partly hydrolysed to glycollic acid and partly converted into aminoacetonitrile; the latter then reacts with the former to produce, ultimately, iminodiacetic acid and nitrilotriacetic acid.

A good yield of glycollic acid can be obtained by distilling with steam the mixture of potassium cyanide and formaldehyde five to ten minutes after mixing. C. S.

Syntheses by means of Mixed Organo-metallic Derivatives of Zinc. α-Halogenated Ketones. Edmond E. Blaise (*Compt. rend.*, 1912, 155, 46—49. Compare this vol., i, 232).—Chlorinated ketones cannot be prepared by the action of α-chlorinated acid chlorides on organo-metallic derivatives of zinc, the principal product of this reaction being a chlorinated ester of a tertiary alcohol. The required result is, however, obtained by the preparation of the *cyclo*acetals and subsequent hydrolysis.

$R\cdot CHCl\cdot CO_2\cdot CMe_2\cdot COCl + R'ZnI =$ 

 $+ H_2O = CMe_2(OH)\cdot CO_2H + R\cdot CHCl\cdot CO\cdot R'$

α-Hydroxy*iso*butyric acid when warmed on a water-bath with chloroacetyl chloride and thionyl chloride yields *α-chloroacetoxy*iso*butyryl chloride*, $CH_2Cl\cdot CO_2\cdot CMe_2\cdot COCl$, b. p. 97°/12 mm., which gives an *anilide*, m. p. 127·5°. The *acid* has m. p. 75°. The acid chloride condenses with zinc *n*-propyl iodide, giving the cyclo*acetal*, $C_9H_{15}O_3Cl$, b. p. 110·5/12 mm., which on hydrolysis with a mixture of acetic and hydrochloric acids gives a good yield of *chloromethyl* n-*propyl ketone*, $CH_2Cl\cdot COPr$, b. p. 154·5—156° or 58—59°/17 mm. Its *semicarbazone* has m. p. 157°.

*Ethyl α-chloro-*n*-propyl ketone*, $CHEtCl\cdot COEt$, b. p. 53°/17 mm., is similarly prepared, starting with *$\alpha\alpha$-chlorobutoxy*iso*butyric acid*, m. p. 61—62°, and condensing its *chloride*, b. p. 106°/11 mm., with zinc ethyl iodide and then hydrolysing the cyclo*acetal*, b. p. 118·5°/12 mm. The above acid chloride gives an *anilide*, m. p. 65—66°. W. G.

The Photochemical Synthesis of Carbohydrates Under the Action of Ultra-violet Rays. Julius Stoklasa, Johann Šebor, and Wenzel Zdobnický (*Biochem. Zeitsch.*, 1912, 41, 333—372).—The photochemical action by means of which carbohydrates are produced from carbon dioxide may, in the view of the authors, be represented by the following equations, according to which both formic acid and aldehyde are formed as intermediate products:

(1) $K_2CO_3 + CO_2 + H_2O = 2KHCO_3$.
(2) $2KHCO_3$ (in light) $= K_2CO_3 + H\cdot CO_2H + O$.
(3) $H\cdot CO_2H$ (in light) $= H\cdot CHO + O$.
(4) $nH\cdot CHO = (H\cdot CHO)_n$.

Each reaction has been studied separately by exposure of the various substances to ultra-violet light in an apparatus which is figured in the text. The formaldehyde polymerises in the presence of alkali to a sugar. The reactions, which involve the setting free of oxygen, have been studied in the presence of nascent hydrogen and ferrous sulphate, which in consequence of their reducing properties facilitate the reaction. The sugars formed are hexoses, of which the phenylosazones melt at 204—205°. They appear to consist of ketones and aldoses,

are optically inactive, do not ferment with yeast, and are not degraded by bacteria which assimilate atmospheric nitrogen.

S. B. S.

Inositol Hexaphosphate. ANGELO CONTARDI (*Gazzetta*, 1912, 42, i, 408—418. Compare Abstr., 1911, i, 157, 609).—Inositol hexaphosphate is obtained by the action of phosphoric acid, D 1·7, on inosite at 120—130° in the absence of air. This compound is probably identical with that obtained from seeds, as the analysis of both compounds, when dried at 120° in hydrogen under 20 mm. pressure, is the same. The anomalies observed in titration are attributed to the formation of complex salts. C. H. D.

Phytin and Phosphoric Acid Esters of Inositol. R. J. ANDERSON (*J. Biol. Chem.*, 1912, 11, 471—488).—The following salts of phytin have been prepared: Tribarium phytate,

$$C_6H_{12}O_9[Ba(PO_3H_2)_2]_3,$$

is obtained pure as an amorphous, colourless powder by repeatedly precipitating barium phytate in 0·5% hydrochloric acid with a like volume of alcohol.

Pentabarium phytate, $C_6H_{14}O_{27}P_6Ba_5$, is obtained when a solution of tribarium phytate in 0·5% hydrochloric acid is neutralised with barium hydroxide and then made faintly acid with acetic acid; it is a colourless, amorphous powder.

Pentabarium ammonium phytate, $C_6H_{12}O_{27}P_6Ba_5(NH_4)_2$, obtained by digesting the tribarium salt with dilute ammonia, forms a heavy, colourless, amorphous powder neutral to litmus.

Pentamagnesium ammonium phytate, $C_6H_{12}O_{27}P_6Mg_5(NH_4)_2$, is formed on adding excess of magnesia mixture to phytic acid; it is a fine colourless, amorphous powder.

Tetracupric dicalcium phytate, $C_6H_{12}O_{27}P_6Cu_4Ca_2$, is obtained when a slightly acid solution of calcium ammonium phytate is precipitated with excess of copper acetate; it constitutes a light blue, amorphous powder.

Phytin is not decomposed on keeping or on heating to 115°.

Experiments made to synthesise phytic acid and inositol hexaphosphoric acid ester led only to the *tetraphosphoric acid* ester,

$$C_6H_6(OH)_2O_4[PO(OH)_2]_4.$$

This is conveniently isolated by means of its barium salt; it is a well characterised compound very similar in appearance and reactions to phytic acid. By heating with acids, inositol and phosphoric acid are regenerated. It gives a colourless precipitate with ordinary molybdate solution or with excess of silver nitrate. E. F. A.

The Higher Carbohydrates Derived from Dextrose. L. H. PHILIPPE (*Ann. Chim. Phys.*, 1912, [viii], 26, 289—418)—A résumé (compare Abstr., 1909, i, 136; 1911, i, 12, 112, 605). Besides the sugars, the alcohols, lactones, and acids of the series have been studied in detail and their physical properties established. Not one of the sugars derived from dextrose is fermented by yeast. There is no regular variation in the physical properties with an increase in the

number of carbon atoms, each carbohydrate having an individuality of its own. E. F. A.

The Reaction between Dextrose and Phenylmethylhydrazine. CARL NEUBERG (*Ber.*, 1912, 45, 1853).—The author's statement that dextrose does not form an osazone with phenylmethylhydrazine under the ordinary conditions of performing the test (Abstr., 1905, i, 90, etc.) in no wise disagrees with the statement that reaction may occur under protracted digestion of the reagents (Buchner and Meisenheimer, this vol., ii, 671). D. F. T.

The Physico-chemical Basis of the Seliwanoff Lævulose Reaction. ADOLF JOLLES (*Biochem. Zeitsch.*, 1912, 41, 331—332).—Königsfeld (this vol., i, 163) has recently shown that dextrose on treatment with hydrochloric acid yields the Seliwanoff lævulose reaction and has ascribed this fact to the change of dextrose into lævulose. The author does not think this explanation is sufficient, for no change could be detected in the rotation after such treatment. He also shows that when dextrose is treated with very dilute alkalis, there is a formation of acid products. S. B. S.

Sugar Solutions and Lime. JULIUS WEISBERG (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 808—811).—Ginnecken has pointed out that when calcium hydroxide and sucrose solutions are mixed at 80° there is no precipitation of trisucrate, but that when the mixture is made at the ordinary temperature there is a loss in the polarisation due to precipitation of trisucrate. This fact is well known, but it has no practical significance, as the separated juice after treatment of the crude juice with lime is not immediately filtered, being first saturated with carbon dioxide gas. E. F. A.

Deflocculation of Starch. GIOVANNI MALFITANO and [Mlle.] A. MOSCHKOFF (*Bull. Soc. chim.*, 1912, [iv], 11, 606—612).—The authors consider that the system water–starch is never a solution, but always a hydrogel or a hydrosol. By a method of estimation by filtration they arrive at the conclusion that, for a given quantity of starch, the greater the quantity of water used, the higher the temperature to which the system is raised and the longer the time of heating the greater is the number of minute particles (that is, particles which persistently pass through a fine filter paper) formed at the expense of the larger ones. W. G.

Conversion of Starch into Dextrin by *X*-Rays. H. A. COLWELL and S. RUSS (*Proc. Phys. Soc., London*, 1912, 24, 217—221; *Le Radium*, 1912, 9, 230—232).—When starch solutions are exposed for several hours to *X*-rays of moderate penetrating power, the opacity and viscosity of the solutions are markedly diminished, and there is a partial conversion into soluble starch and dextrin.

Dextrin under similar conditions could not be converted into dextrose. The effect is attributed to a direct action on the starch molecules, either by the *X*-rays or by the secondary rays which they produce. E. F. A.

Gums and Mucilages. WOLFGANG SCHIRMER (*Arch. Pharm.*, 1912, **250**, 230—251).—The gum obtained from *Anogeissus latifolius* dissolves not quite completely in water, and is very sparingly soluble in glacial acetic acid or 96% alcohol. It is completely soluble in a 60% or 80% solution of chloral hydrate, more easily in the former than in the latter. It yields mucic acid by oxidation with nitric acid, D 1·15, and 26·25% of pentosan and 7·64% of methylpentosan by distillation with 12% hydrochloric acid at 140—150°. By hydrolysis with dilute sulphuric acid on the water-bath for ten hours, the gum yields *l*-arabinose and *d*-galactose. The gum from *Odina Wodier* yields furfuraldehyde by distillation with 12% hydrochloric acid, mucic acid by oxidation with nitric acid, and *d*-galactose and *l*-arabinose by hydrolysis with dilute sulphuric acid.

Both of these gums, therefore, consist largely of arabo-galactans, but in the former the araban, in the latter the galactan, predominates. The mucilage obtained from the pith of *Sassafras variifolium* is purified by repeated maceration with water, decantation, and precipitation from the aqueous solution by alcohol. The purified material is a white, light substance which swells, but is insoluble, in water; also it does not dissolve in other solvents, in dilute acids or alkalis, or even in an 80% solution of chloral hydrate. By oxidation with nitric acid, it yields saccharic acid, but not mucic acid, whilst by hydrolysis with dilute sulphuric acid, it is converted into *l*-arabinose and dextrose, the former in the larger quantity.

The mucilage obtained from the roots of *Althaea officinalis* is partly soluble in water, insoluble in chloral hydrate or ammoniacal cuprous oxide solution, and dissolves almost entirely in boiling acids. The mucilage contains pentosans (identified by the formation of furfuraldehyde), yields mucic acid and a very little saccharic acid by oxidation with nitric acid, and is converted by hydrolysis with dilute sulphuric acid mainly into dextrose, galactose and a small quantity of a pentose also being formed.

The mucilage obtained from the bark of *Ulmus fulva* is insoluble in most solvents, but dissolves partly in dilute acids. It contains about 60% of pentosans, methylpentosans, and hexosans, the last yielding galactose, lævulose, and dextrose by hydrolysis. C. S.

Preparation of Large Crystals of Betaine Periodide. VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm*, 1912, **36**, 577).—A betaine salt is kept in a loosely-closed vessel containing 10% potassium iodide in 10% sulphuric acid, potassium iodide being run in as long as the precipitate first formed dissolves again. In the course of a week, oxidation has been brought about by the atmosphere, and very large crystals of the betaine periodide separate out. E. F. A.

Compounds of Alkali and Alkali-earth Salts with Organic Bases. FILIPPO CALZOLARI (*Atti R. Accad. Lincei*, 1912, [v], **21**, i, 563—569. Compare Barbieri and Calzolari, Abstr., 1911, i, 184, 266, 268).—The following compounds of salts, mostly hydrated, with hexamethylenetetramine have been prepared: $LiI,4H_2O,C_6H_{12}N_4$; $NaCNS,4H_2O,C_6H_{12}N_4$; $NaClO_4,H_2O,C_6H_{12}N_4$; $2NH_4CNS,C_6H_{12}N_4$;

$2KCNS,C_6H_{12}N_4$; $CaCl_2,10H_2O,C_6H_{12}N_4$; $CaBr_2,10H_2O,2C_6H_{12}N_4$; $CaI_2,10H_2O,2C_6H_{12}N_4$; $Ca(NO_3)_2,3H_2O,C_6H_{12}N_4$; $SrCl_2,10H_2O,2C_6H_{12}N_4$; $SrBr_2,10H_2O,2C_6H_{12}N_4$; $SrI_2,10H_2O,2C_6H_{12}N_4$; $SrI_2,12H_2O,4C_6H_{12}N_4$, and $Ba(CNS)_2,6H_2O,2C_6H_{12}N_4$. All of these salts are crystalline, and do not deliquesce in air. The following compounds with caffeine have also been prepared: $SrI_2,H_2O,2C_8H_{10}O_2N_4$; $NaClO_4,C_8H_{10}O_2N_4$; $2KCNS,C_8H_{10}O_2N_4$. C. H. D.

Compound Obtained by Treating Carbamide with Formaldehyde. STEFANO DI PALMA (*Boll. Chim. Farm.*, 1912, **51**, 78—79).—The interaction of carbamide and formaldehyde in aqueous solution yields the *compound*, $C_2H_6O_2N_2$ or $CO(NH_2)_2.CH_2O$, as a white, amorphous, odourless, and tasteless powder, which decomposes at 245°. With boiling concentrated sodium hydroxide solution, it yields ammonia, and concentrated sulphuric acid in the hot dissolves it with formation of a red coloration and evolution of gas; with hot dilute hydrogen chloride, it yields aldehyde vapour. When suspended in water and distilled in a current of steam, it is decomposed into its constituents. T. H. P.

Cyanamide. I. Cyanamide and Ethyl Acetoacetate. ADOLF SONN (*Ber.*, 1912, **45**, 1958—1960. Compare Brigl, this vol., i, 533).—Ethyl β-cyanoaminocrotonate has been obtained by the interaction of sodium cyanamide and ethyl acetoacetate; it is unstable, decomposing to a pale yellow oil.

With mercuric chloride, a *compound*, $(C_7H_{10}O_2N_2)_2,HgCl_2$, is obtained in slender, lustrous needles, m. p. 101°.

Disodium cyanamide and ethyl diethylacetoacetate interact to form ethyl *iso*carbopyrotritarate.

Monosodium cyanamide and ethyl diethylacetoacetate yield *ethyl 1-cyano-2:5-dimethylpyrrole-3:4-dicarboxylate*, $CN\cdot N<\begin{matrix}CMe:C\cdot CO_2Et\\ \vert \\ CMe:C\cdot CO_2Et\end{matrix}$; it forms crystals, m. p. 166°.

Cyanamide salts readily interact with compounds containing acid methylene hydrogen. E. F. A.

Preparation of Ammonia and Formic Acid from Calcium Cyanamide. H. SULZER (*Zeitsch. angew. Chem.*, 1912, **25**, 1268—1273).—Calcium cyanamide reacts with carbon according to the equation $CaCN_2 + C \rightleftharpoons Ca(CN)_2$, but at the high temperature required for fusion, very little cyanide is formed. The melting point may be lowered by addition of alkali salts, when the reaction becomes $CaCN_2 + C + 2NaCl = CaCl_2 + 2NaCN$ or $CaCN_2 + C + Na_2CO_3 = CaCO_3 + 2NaCN$. The best results are obtained by mixing one hundred parts of calcium cyanamide, twenty parts of wood charcoal, and seventy-five to ninety parts of anhydrous sodium carbonate, and heating to whiteness in a closed iron crucible for fifteen to twenty minutes.

The hydrolysis of hydrogen cyanide to ammonia and formic acid may be utilised technically in the following manner. The ground product obtained as above is mixed with fifty to sixty times its quantity of water, and heated to 170° in an enamelled iron autoclave. The temperature is then raised to 190° for ten minutes, after which

the product is distilled. Ammonia is recovered from the distillate, and the residue contains sodium formate.

Formic acid is most conveniently detected in presence of hydrochloric acid by its reaction with a mixture of potassium dichromate solution and concentrated sulphuric acid, when reduction occurs, yielding a green solution. C. H. D.

The Constitution of the Fulminuric Acids. V. Breaking Down of Furoxandicarboxylamide. CELSO ULPIANI (*Gazzetta*, 1912, 42, i, 375—390).—The amide obtained by the action of ammonia on the product of nitration of ethyl acetoacetate (Ulpiani and Bernardini, Abstr., 1904, i, 971; 1905, i, 750: Wahl, Abstr., 1908, i, 140) is boiled with an excess of water, and is converted into β-fulminuramide, γ- and ordinary fulminuric acids, and carbamide.

β-Fulminuramide, $C_3H_4O_2N_4$, crystallises from water in plates, m. p. 175°, and is not decomposed by dilute acids. It does not react with ferric chloride. It is hydrolysed by barium hydroxide, yielding β-fulminuric acid, $C_3H_3O_3N_3$, which is also stable, and has m. p. 196°. The ethyl ester has m. p. 103—104°. The *nitroso*-derivative, $C_3H_2O_3N_3,H_2O$, explodes at 133°, and yields the ammonium salt of oximinocyanoacetic acid with ammonia. The formula

$$\mathrm{NH}\Big\langle\begin{array}{l}\mathrm{CH{-}C{\cdot}CO_2H}\\ \mathrm{N{\cdot}O{\cdot}N}\end{array}$$

is assigned to the acid.

γ-Fulminuric acid crystallises from water, m. p. 247°, and does not form a nitroso-compound. The *silver* salt has been analysed. Barium hydroxide removes ammonia, and a *barium* salt, $C_3O_4N_2Ba,3H_2O$, is formed, from which *4-nitro-5-hydroxy*iso*oxazole*, $\mathrm{N}\Big\langle\begin{array}{l}\mathrm{CH{\cdot}C{\cdot}NO_2}\\ \mathrm{O\,{-}\,C{\cdot}OH}\end{array}$, m. p. 125°, is obtained by means of acids. This acid crystallises with H_2O, and yields a *diammonium* salt, $C_3H_8O_4N_4$.

γ-Fulminuric acid is thus regarded as 4-*nitro*-5-*amino*iso*oxazole*, $\mathrm{N}\Big\langle\begin{array}{l}\mathrm{CH{\cdot}C{\cdot}NO_2}\\ \mathrm{O\,{-}\,C{\cdot}NH_2}\end{array}$, and a scheme is then given for the breaking down of the original amide. C. H. D.

The Constitution of the Fulminuric Acids. VI. Liebig's Fulminuric Acid. CELSO ULPIANI (*Gazzetta*, 1912, 42, i, 390—408). —The constitution of Liebig's fulminuric acid is discussed. If ammonium fulminurate is suspended in alcohol, and a stream of dry hydrogen chloride passed through it, nitromalonamide and the ammonium salt of ethyl nitromalonate are obtained:

$$NO_2H{:}C(CN){\cdot}CO{\cdot}NH_2 \longrightarrow NO_2H{:}C(CO{\cdot}NH_2)_2 \longrightarrow NO_2H{\cdot}C(CO_2Et)_2.$$

[With LUIGI BERNARDINI.]—Determinations of the electrical conductivity of fulminuric acid in aqueous solution show that the strength of the acid approaches that of nitric acid, whilst the replacement of the cyano-group by the group $-CO{\cdot}NH_2$, in nitromalonamide, greatly diminishes the strength. The conductivity of the ammonium salts increases in the order of the substituting groups: $(CO_2Et)_2$, $(CO{\cdot}NH_2)_2$, $(CN)(CO_2Et)$, $(CN)(CO{\cdot}NH_2)$.

Alcoholic ammonia reacts with ethyl nitrocyanoacetate in a sealed tube at 140°, yielding a crystalline compound, $C_5H_{10}O_8N_4,\frac{1}{2}H_2O$, which has a low conductivity, and evolves ammonia when warmed with sodium carbonate. The constitution is uncertain. C. H. D.

The Binary Systems of Potassium and Sodium Cyanides with the Corresponding Salts of Silver, Copper, and Zinc, and with Potassium and Sodium Chlorides. WILHELM TRUTHE (*Zeitsch. anorg. Chem.*, 1912, 76, 129—160).—The cyanides are fused in an atmosphere of nitrogen, dried and freed from oxygen, and the thermocouple is protected by means of a glass capillary.

Potassium cyanide has m. p. 622°, and sodium cyanide, m. p. 561·7°, both salts being previously dried in nitrogen at 150°. The absorption of oxygen, forming cyanates, lowers the m. p. The two salts form a continuous series of solid solutions, the freezing-point curve passing through a minimum at 502°. A transformation takes place in the solid crystals at 260°, reaching a maximum at about the ratio 1 : 1. As a similar transformation has been observed in the pairs $NaBO_2$–KBO_2, NaCl–KCl, and NaCl–LiCl, it is probable that a compound is formed. The change takes place on cooling with development of heat and contraction of volume.

Potassium cyanide and potassium chloride form a continuous series of solid solutions, and the crystals become turbid in course of time, although a thermal effect cannot be detected. Sodium cyanide and sodium chloride form an exactly similar series.

Potassium and silver cyanides form a stable double salt,

AgCN,KCN,

giving rise to a maximum on the freezing-point curve at 370°. As silver cyanide melts with decomposition at 320—350°, the mixtures are best studied by preparing the double salt in the wet way, and then melting it with excess of the one or the other salt. Decomposition is thus avoided. The curve has two eutectic points, both at about 290°, and the form of the maximum indicates that the double salt is very little dissociated on fusion. Solid solutions are not formed. Microscopical examination confirms the thermal results.

The compound AgCN,NaCN, prepared in the wet way, has m. p. 471°, with some decomposition. Mixtures richer in silver cyanide decompose readily, and the freezing-point curve is incomplete on that side. There is a eutectic point at 422°, and two series of solid solutions are formed.

Cuprous cyanide melts without much decomposition at 473°, and forms a complex system with potassium cyanide. Three compounds are formed from the liquid: $KCN,Cu_2(CN)_2$, which gives a maximum at 327°; $2KCN,Cu_2(CN)_2$, giving a flat maximum at 327°, and $6KCN,Cu_2(CN)_2$, which is indicated by a break in the freezing-point curve at 400°. Solid solutions are not formed. In addition to these, two compounds are produced by reactions in the solid state:

$$2KCN,3Cu_2(CN)_2$$

at 230°, and $3KCN,Cu_2(CN)_2$ at about the same temperature.

Cuprous cyanide and sodium cyanide form a system of unusual type. There are four compounds, of which two, $4NaCN,Cu_2(CN)_2$ and

$6NaCN,Cu_2(CN)_2$, form a continuous series of solid solutions with both components. The third, $2NaCN,Cu_2(CN)_2$, has m. p. 398°, and occurs as a maximum on the curve, whilst the fourth,

$$3NaCN,Cu_2(CN)_2,$$

is formed in the solid state at 318°.

Zinc cyanide is infusible, and only decomposes slowly at 1000°. The compound $2KCN,Zn(CN)_2$ has a maximum m. p. 538°. Solid solutions are not formed, but the system has not been completely investigated, owing to extensive decomposition. This is still more marked in mixtures of sodium and zinc cyanides, and in mixtures of zinc and cuprous cyanides.

There is no necessary relation between the compounds which separate from molten mixtures and those which crystallise from aqueous solution, but the formulæ are in most cases the same.

C. H. D.

Influence of Oxidising Agents on the Rate of Solution of Gold in Potassium Cyanide. JAKOV I. MICHAILENKO and M. I. MESHTSCHERJAKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 567—570).—The dissolution of gold by potassium cyanide solution requires the presence of an oxidising agent, and is retarded or entirely prevented by the introduction of hydrogen ions into the solution. Hydroxyl ions do not favour the dissolution, and in excess may exert a retarding influence. In a neutral medium (that is, one to which neither acid nor alkali has been added) the rate of solution of the metal is not appreciably affected by the following oxidising agents: quinone, $Na_2SnO_3 + 3H_2O$, $KBrO_3$, KIO_3, $KClO_3$, $Hg(CN)_2$, $CuCl_2 + 2H_2O$; it is, however, accelerated by $KClO_4$, $KMnO_4$, KIO_4, NH_4SO_4, Na_2O_2, KSO_4, $NaSO_4$, Br, $K_3Fe(CN)_6$, or KCO_3. The relative accelerations produced by these oxidising agents in centi-normal concentration are as follows: $KClO_4$, 1; KIO_4, 2; KCO_3, 2; NH_4SO_4, 3; KSO_4, 4; $NaSO_4$, 4; Na_2O_2, 4, and $K_3Fe(CN)_6$, 5. The velocity of solution of the gold is increased by increase of the concentration of the oxidising agent to a certain limit, and may be diminished by further addition. The combined action of two oxidising agent present together is less than that of the more effective of them. The addition to potassium cyanide of NaCl, $Hg(CN)_2$, $CuCl_2$, or $CoCl_2$ has either no influence or a retarding one on the rate of solution of gold.

T. H. P.

Mercuric Oxycyanide. III. ERWIN RUPP and S. GOY (*Arch. Pharm.*, 1912, **250**, 280—290).—*Mercuric cyanide sulphate*,

$$Hg(CN)_2,HgSO_4,5H_2O,$$

stout needles, is obtained by evaporating a solution of mercuric oxycyanide or of equal molecular quantities of mercuric cyanide and sulphate in dilute sulphuric acid. It is decomposed by water into mercuric cyanide and basic mercuric sulphate.

The following double salts have been prepared by dissolving mercuric oxycyanide in the requisite acid—in the case of the organic acids, in the absence of water: *cyanide nitrate*, $Hg(CN)_2,Hg(NO_3)_2$, colourless plates; *cyanide acetate*, $Hg(CN)_2,Hg(OAc)_2$, slender needles; *cyanide*

formate, $Hg(CN)_2,Hg(HCO_2)_2$, prisms; *cyanide oxalate*,

$$Hg(CN)_2,Hg(CO_2)_2,$$

microcrystalline powder; *cyanide succinate*,

$$Hg(CN)_2,HgC_4H_4O_4,2H_2O,$$

long prisms; *cyanide benzoate*, $Hg(CN)_2,Hg(OBz)_2\,H_2O$, long prisms, all of which are decomposed by water.

Whilst mercuric cyanide forms clear solutions with aqueous ammonia and ammoniacal compounds, mercuric oxycyanide yields precipitates. The oxycyanide behaves like a mixture of mercuric cyanide and mercuric oxide, so that in the reaction with ammoniacal compounds the solutions contain mercuric cyanide, whilst the precipitates consist of mercuriammonium compounds.

The whole behaviour of solid mercuric oxycyanide is expressed by the formula $Hg(CN)_2,HgO$. Its molecular weight in solution (and also that of the cyanide acetate), determined by the cryoscopic method, corresponds with the formula $OH\cdot Hg\cdot CN$ (or $OAc\cdot Hg\cdot CN$), but this is probably due to dissociation; evidence for the existence of an ion, $\cdot Hg\cdot CN$, has not been obtained. C. S.

Transformation of Ferricyanic Acid into Ferrocyanic Acid and the Hydrolysis of Ferric, Zinc, and Aluminium Chlorides. Cam. Gillet (*Bull. Soc. chim. Belg.*, 1912, **26**, 236—238).—The reaction $2H_4Fe(CN)_6 + Cl_2 + aq \rightleftharpoons 2H_3Fe(CN)_6 + 2HCl + aq$ is shown to be reversible. Hydrochloric or hydrobromic acids convert ferricyanic acid into ferrocyanic acid with the liberation of chlorine or bromine. When the acid is neutralised by a strong base there is complete conversion from ferrocyanide into ferricyanide. When the chlorine is removed as it is formed, complete conversion into ferrocyanic acid is effected. This may be done with reduced silver for the chlorine, or phenol or chloroform for the bromine. Instead of the acids, the chlorides or bromides of iron, zinc, or aluminium may be used with the same result; this indicates that these chlorides are hydrolysed in solution.

The chlorine liberated in the interaction between potassium ferricyanide and ferric chloride is not produced by the dissociation of the latter into ferrous chloride and chlorine, but it is due to the oxidation of the hydrochloric acid of the ferric oxide contained in the ferricyanic acid. E. F. A.

Copper Salts of Hydroferrocyanic and Hydroferricyanic Acids. Erich Müller, Gustav Wegelin, and E. Kellerhoff (*J. pr. Chem.*, 1912, **86**, [ii], 82—111).—The authors have investigated the composition of the precipitates formed by the interaction of cupric sulphate and cuprous chloride with potassium ferrocyanide, potassium ferricyanide, hydroferrocyanic acid, and hydroferricyanic acid in various proportions in 0·1 molar aqueous solution. The composition of the precipitates was deduced by determining the amounts of Cu'', Cu', $Fe''(CN)_6$, and $Fe'''(CN)_6$ remaining in the solution.

From theoretical considerations it is shown that the precipitate formed by mixing solutions containing equivalent amounts of cupric and ferrocyanogen ions should have the same composition

as that obtained from solutions containing the same equivalent amounts of cuprous and ferricyanogen ions, and this conclusion is confirmed by the authors' experimental results.

The greenish-brown precipitate formed from cupric sulphate and potassium ferricyanide has the same composition, $Cu_3''[Fe'''(CN)_6]_2$, for all values of the ratio $CuSO_4/K_3Fe'''(CN)_6$.

With cupric sulphate and potassium forrocyanide, the precipitate has a constant composition only when one of the two components is in great excess; for values of the ratio $CuSO_4/K_4Fe''(CN)_6(=w)$ in the neighbourhood of 0·1, a brown precipitate which changes to yellow and has the composition $K_2Cu''Fe''(CN)_6$ is produced, whilst if $w > 2{\cdot}5$ a brown precipitate of $Cu_2''Fe''(CN)_6$ is obtained. When $w = 1{\cdot}5$ the precipitate consists of $K_2Cu_3''[Fe''(CN)_6]_2$. For values of $w = 0{\cdot}1$—$1{\cdot}5$ a mixture of $K_2Cu''Fe''(CN)_6$ and $K_2Cu_3''[Fe''(CN)_6]_2$ is formed, whilst for values $= 1{\cdot}5$—$2{\cdot}5$ the precipitate consists of a mixture of the latter compound with $Cu_2''Fe''(CN)_6$.

When $w < 1{\cdot}5$ the solution contains a small amount of ferricyanide, probably produced as follows:

$$2K_2Cu''Fe''(CN)_6 = KCu'Cu''Fe''(CN)_6 + K_3Fe'''(CN)_6.$$

Similar results were obtained with solutions of sodium ferrocyanide and cupric sulphate.

In the case of cupric sulphate and hydroferrocyanic acid the brown precipitate has the composition $Cu_2''Fe''(CN)_6$ for all values of the ratio $CuSO_4/H_4Fe''(CN)_6(=x)$ above 2; when x is approximately 0·5 the precipitate consists of $H_2Cu_3''[Fe''(CN)_6]_2$, whilst for values of $x = 0{\cdot}5$—2 a mixture of the latter compound with $Cu_2''Fe''(CN)_6$ is produced.

With solutions of potassium ferrocyanide and cuprous chloride dissolved in aqueous sodium chloride, the white precipitate has the composition $K_2Cu_2'Fe''(CN)_6$ when the ratio $CuCl/K_4Fe''(CN)_6(=y) < 2$. For values of $y > 3{\cdot}5$ the precipitate consists of $KCu_3'Fe''(CN)_6$, whilst for intermediate values (2—3·5) a mixture of these two substances is formed.

Similar results were obtained with solutions of hydroferrocyanic acid and cuprous chloride dissolved in hydrochloric acid.

The precipitates formed by mixing solutions of cuprous chloride and potassium ferricyanide consist of ferrocyanides and not ferricyanides. For values of the ratio $CuCl/K_3Fe'''(CN)_6(=z) < 1$, a mixture of $K_2Cu_3''[Fe''(CN)_6]_2$ and $K_2Cu''Fe''(CN)_6$ is produced. As z becomes > 1, the latter compound is gradually replaced by $K_2Cu_2'Fe''(CN)_6$ until $z = 1{\cdot}75$, when the precipitate consists only of $K_2Cu_2'Fe''(CN)_6$ and $K_2Cu_3''[Fe''(CN)_6]_2$.

As z increases from 1·75 to 2, the two last-mentioned compounds are accompanied by $KCuCu_3''[Fe''(CN)_6]_2$. For still greater values of z the precipitate consists of a mixture of $KCu_3'Fe''(CN)_6$, $K_2Cu_2'Fe''(CN)_6$, and $KCu'Cu_3''[Fe''(CN)_6]_2$. Only when the cuprous chloride is in great excess ($z > 10$) has the precipitate a definite composition, namely, $KCu_3'Fe''(CN)_6$. The latter compound is obtained as a white precipitate by dropping aqueous potassium ferrocyanide into the cuprous chloride solution. F. B.

Stereochemistry of the Aromatic Series. ROMÁN CASARES (*Anal. Fis. Quim*, 1912, 10, 150—152).—Polemical against Lozano (compare this vol., i, 430). G. D. L.

The Study of Hydro-aromatic Substances. EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1911, 99—101).—An account of the synthesis of 1 : 1 : 3-trimethyl*cyclo*hexene (Trans., 1910, 97, 2218) and 1 : 1 : 2-trimethyl*cyclo*hexan-3-one (Trans., 1911, 99, 1101). C. H. D.

Possible Existence of Cyclic Hydrocarbons Containing Nuclear Triple Linkings. ALEXEI E. FAWORSKY and W. BOSHOWSKY (*Annalen*, 1912, 390, 122—129).—The authors have unsuccessfully attempted to prepare a cyclic hydrocarbon containing a nuclear triple linking.

By bromination in cold chloroform, chloro-Δ^1-*cyclo*hexene yields 1-*chloro*-1 : 2-*dibromo*cyclo*hexane*, $C_6H_9ClBr_2$, m. p. 43—44°, which is converted by alcoholic potassium hydroxide into chloro-Δ^1-*cyclo*hexene and 1 : 2-*dibromo*-Δ^1-cyclo*hexene*, $C_6H_8Br_2$, m. p. 39—40°, b. p. 90—92°/6 mm. The latter, the constitution of which is proved by its oxidation to adipic acid, is unattacked by zinc dust, copper, silver, calcium, or amalgamated zinc and aluminium, but in ethereal solution is converted by sodium into a mixture of dodecahydrotriphenylene (Mannich, Abstr., 1907, i, 205) and a viscous substance which is not attacked by potassium permanganate. So far as the six-membered ring is concerned, therefore, the existence of a hydrocarbon containing a nuclear triple linking has been disproved. C. S.

The Study of Isomorphous Sulphonic Derivatives of Benzene. HENRY A. MIERS, HENRY E. ARMSTRONG, WILLIAM J. POPE, and WILLIAM P. WYNNE (*Brit. Assoc. Report*, 1911, 82—83. Compare Colgate and Rodd, Trans., 1910, 97, 1585). C. H. D.

Conversion of Carbazole into Dimethyl-di-*cyclo*pentyl, a Hydrocarbon Present in Petroleum. JULIUS SCHMIDT and AUGUST SIGWART (*Ber.*, 1912, 45, 1779—1787).—When carbazole is heated at 130° with hydrogen iodide and phosphorus, hexahydrocarbazole is obtained in almost theoretical proportion. At 200—240°, the main product is a hydrocarbon, $C_{12}H_{22}$ (compare Graebe and Glaser, Abstr., 1872, 302). On oxidation with nitric acid, butyric acid is obtained, and the compound is regarded as 3 : 3′-*dimethyldi*cyclo*pentyl*. It has b. p. 213—214°/738 mm., D^{20} 0·8784, n_D^{25} 1·4730, figures which are in close agreement with those given by a hydrocarbon, $C_{12}H_{22}$, obtained from Louisiana petroleum by Coates (Abstr., 1906, i, 329).

Hexahydrocarbazole forms colourless, silky, lustrous needles, m. p. 99°.

9-*Methylhexahydrocarbazole methiodide*, obtained on heating the carbazole with methyl iodide and methyl alcohol, crystallises in octahedral or cubic crystals, m. p. 194—195° (decomp.). On heating it, 9-*methylhexahydrocarbazole* is obtained as a mobile, colourless liquid,

b. p. 294—295°/748 mm, D_4^{19} 1·035, n_D^{19} 1·6248. The *picrate* forms pale yellow platelets, m. p. 143—144° (decomp.); the *picrolonate* separates in pale yellow, silky needles, m. p. 174—175°.

*Dimethyldi*cyclo*pentyl* is a transparent, mobile liquid, with a marked odour of petroleum. E. F. A.

Colloidal Palladium. Partial and Total Hydrogenation of Phenylacetylene, Tolane, and Diphenyldiacetylene. CHR. KELBER and ANTON SCHWARZ (*Ber.*, 1912, **45**, 1946—1952).—Colloidal palladium, which is active in glacial acetic acid and is not destroyed by dilute mineral acids, is prepared as follows. Gluten is heated with acetic acid, and to the solution is added palladous chloride dissolved in a little water. The clear, dark brown solution is faintly basified with ammonia, and then slowly treated with hydrazine hydrate. After the completion of the reaction, the deep, brownish-black liquid is dialysed until free from chlorine, and is then carefully evaporated, finally to dryness in a vacuum. The product forms black, glistening lamellæ, and is easily soluble in water or glacial acetic acid; the solutions are not rendered flocculent by dilute mineral acids. The substance contains about 17·2% of palladium.

By passing the calculated amounts of hydrogen through their solutions in glacial acetic acid containing 0·1 gram of the colloidal palladium, phenylacetylene has been reduced to styrene or ethylbenzene, tolane to stilbene and *iso*stilbene or dibenzyl, and diphenyldiacetylene to *cis-cis-* and *cis-trans-*$\alpha\delta$-diphenyl-$\Delta^{\alpha\gamma}$-butadiene or $\alpha\delta$-diphenylbutane. C. S.

Direct Hydrogenation of Diphenylethanes. Preparation of Di*cyclo*hexylethanes PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1912, **154**, 1771—1773).—Diphenyl and diphenylmethane have both been reduced by direct hydrogenation to the corresponding di*cyclo*hexyl and di*cyclo*hexylmethane (compare this vol., i, 547, and Eykman, Abstr., 1904, i, 26). The authors have extended the reaction to the next higher homologues.

$\alpha\beta$-Diphenylethane when passed with excess of hydrogen over reduced nickel at 160—170° is transformed completely into *αβ-di*cyclo*hexylethane*, $C_6H_{11}\cdot CH_2\cdot CH_2\cdot C_6H_{11}$, a colourless liquid, b. p. 270—271° (corr.); D_4^{18} 0·8838; n_D^{18} 1·480. It is not attacked by a mixture of nitric and sulphuric acids.

$\alpha\alpha$-Diphenylethane is much more difficult to reduce. When its vapour is passed with excess of hydrogen over reduced nickel at 170°, the product formed is *α-phenyl-α-*cyclo*hexylethane*,

$$CHMePh\cdot C_6H_{11},$$

a colourless liquid with an odour of citron, b. p. 264—266° (corr.), D_4^{17} 0·9773, n_D^{17} 1·549. It is violently attacked in the cold by the nitrosulphuric mixture. This substance when submitted to three successive hydrogenations at 170° is finally reduced to *αα-di*cyclo*hexylethane*,

$$CHMe(C_6H_{11})_2,$$

a colourless liquid, b. p. 256—257° (corr.); D_4^{20} 0·9271; n_D^{20} 1·511. It is not acted on by a mixture of nitric and sulphuric acids.

W. G.

Reaction Differences of Stereoisomeric Ethylene Halides. I. PAUL PFEIFFER (*Ber.*, 1912, **45**, 1810—1819).—It is found that certain stereoisomeric ethylene halides show greater differences in chemical behaviour than would be expected from the ordinary structural conception of the asymmetric carbon atom.

2 : 4-Dinitrostilbene gives two isomeric additive compounds with chlorine; the *α-chloride* (yellow leaflets, m. p. 167°) is obtained by the action of chlorine on the chloroform solution, whilst the *β-chloride* is the main product when the reaction is carried out in carbon disulphide. When heated on the water-bath with pyridine, both these chlorides yield *α-chloro-2 : 4-dinitrostilbene*, $C_6H_3(NO_2)_2\cdot CCl{:}CHPh$, prismatic needles, m. p. 104°; when exposed to light the crystals are reddened, whilst the solution in pyridine gives a nitrophenylisatogen (see next abstract).

The 2 : 4-dinitrostilbene bromides are obtained by the action of bromine on the parent substance in glacial acetic acid, and can be separated by means of alcohol. The α-isomeride forms colourless needles from acetic acid, m. p. 185° (compare Thiele and Escales, Abstr., 1901, i, 689); the *β-isomeride* forms pale yellow leaflets, m. p. 145—146°. Whereas the β-bromide on warming in pyridine solution yields *α-bromo-2 : 4-dinitrostilbene*, yellow tablets, m. p. 98—99°, reddened by light and converted by an aqueous alcoholic solution of sodium hydroxide into dinitrotolane, the α-isomeride under similar treatment with pyridine gives 2 : 4-dinitrostilbene (m. p. 140°).

Stilbene when treated in ethereal solution with chlorine gives a mixture of the α- and β-isomeric chlorides. The α-chloride (needles, m. p. 191—193°) is surprisingly stable, and resists the action of pyridine, even at 200° in a sealed tube, whereas the β-compound (m. p. 93—94°), although more stable than the corresponding dinitrostilbene derivative, gives monochlorostilbene (prismatic needles, m. p. 52—54°).

The stilbene dibromides (compare Wislicenus and Seeler, Abstr., 1896, i, 98) was prepared by the action of bromine on a cold carbon disulphide solution of stilbene. The α-isomeride (m. p. 236°) on treatment with pyridine gives stilbene, whilst the β-compound (m. p. 111°) gives as chief product monobromostilbene. D. F. T.

Rearrangements in Light. PAUL PFEIFFER (*Ber.*, 1912, **45**, 1819—1830).—A pyridine solution of α-chloro-2 : 4-dinitrostilbene, $C_6H_3(NO_2)_2\cdot CCl{:}CHPh$ (compare preceding abstract), on exposure to sunlight soon becomes coloured, due to the formation of an easily isolable red substance.

[With A. FORNET, E. KRAMER, FR. MATZKE, and L. SPIRO.]—In order to discover which of the nitro-groups is affected, *α-chloro-4-nitro-2-cyanostilbene* (yellow, silky needles, m. p. 134°) and *α-chloro-2-nitro-4-cyanostilbene* (yellow leaflets, m. p. 162—163°) were prepared by the action of pyridine at 150—170° on the two corresponding nitrocyanostilbene chlorides, $NO_2\cdot C_6H_3(CN)\cdot CHCl\cdot CPhCl$ (the 4 : 2-compound, colourless needles, m. p. 118—119°; the 2 : 4-compound, colourless leaflets, m. p. 196—197°), which are easily obtained by the action of chlorine on chloroform solutions of the two nitrocyanostilbenes (Ullmann and Gschwind, Abstr., 1908, i, 623). The chloro-2-nitro-

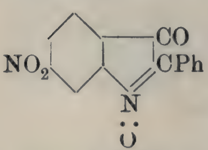
4-cyanostilbene, unlike the isomeride, in pyridine solution is readily affected by light with the formation of an orange-red substance.

2 : 2′-*Dinitrostilbene chloride*, $NO_2 \cdot C_6H_4 \cdot CHCl \cdot CHCl \cdot C_6H_4 \cdot NO_2$, was obtained by the action of chlorine on a chloroform solution of *oo*′-dinitrostilbene (Bischoff, Abstr., 1888, 1094); it forms yellow needles, m. p. 152—153°, and when heated with pyridine at 160—170°, gives *a-chloro*-2 : 2′-*dinitrostilbene*, yellow needles or leaflets, m. p. 124°. The pyridine solution of this last substance is turned orange-red by light. Treatment with alcoholic potash, on the other hand, removes the elements of hydrogen chloride with the formation of *oo*′-dinitrotolane (yellow needles, m. p. 192—193° to a deep red liquid; compare Kliegl and Haas, Abstr., 1911, i, 433). The action of bromine in sunlight on an ethereal solution of dinitrotolane produces a yellow, crystalline *dibromide*, m. p. 217°, which, when crystallised from cold benzene, gives tablets of an unstable additive *compound* with benzene. Dinitrotolane, unlike dinitrostilbene, is readily affected when its pyridine solution is exposed to light.

From the above experimental results, it is probable that the nitro-group in the ortho-position and also the carbon-carbon bond are both implicated in the change produced by light on *a*-chloro-2 : 4-dinitrostilbene, and the conclusion is drawn that the reaction occurs in the steps: $NO_2 \cdot C_6H_3 <\begin{smallmatrix} CCl\colon CHPh \\ NO_2 \end{smallmatrix} \longrightarrow NO_2 \cdot C_6H_3 <\begin{smallmatrix} C\vdots CPh \\ NO_2 \end{smallmatrix} \longrightarrow$

$$NO_2 \cdot C_6H_3 <\begin{smallmatrix} CO- \\ NO \end{smallmatrix}\!\!> CPh,$$

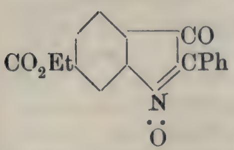
the final product belonging to the isatogen class (Baeyer, Abstr., 1882, 620, etc.), being probably 6-*nitro*-2-*phenylisatogen* (formula annexed; compare Angeli and Angelico, Abstr., 1907, i, 153); it separates from the pyridine solution in red leaflets, m. p. 206°. Sulphur dioxide acting on the acetic acid solution gives a brownish-black *substance* (leaflets), and also yellow leaflets of a substance, m. p. 257—258°, probably 6-*nitro*-2-*phenylindoxyl*.



a-Chloro-2-nitro-4-cyanostilbene can be hydrolysed by hydrogen chloride in alcoholic solution to *ethyl a-chloro-2-nitrostilbene-4-carboxylate*, $CO_2Et \cdot C_6H_3(NO_2) \cdot CCl\colon CHPh$, yellow leaflets, m. p. 98°; this can be hydrolysed by sulphuric acid in 50% acetic acid solution to the free acid, *a-chloro-2-nitrostilbene-4-carboxylic acid*,

$$CO_2H \cdot C_6H_3(NO_2) \cdot CCl\colon CHPh,$$

bright yellow needles, m. p. 186°; sodium salt, yellow needles. The ester when exposed in pyridine solution to sunlight gives *ethyl-2-phenylisatogen-6-carboxylate* (formula annexed), orange needles, m. p. 138°.



D. F. T.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. F. STANLEY KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc.*

Report, 1911, 94—98).—A series of quantitative studies of chlorination of anilides, and of the formation of nitroamines (Trans., 1911, **99**, 1185, 1369, 1377). C. H. D.

Action of Aniline on Uranyl Salts. II. GIUSEPPE INGHILLERI (*Atti R. Accad. Fisiocritici, Siena*, 1911).—Uranylaniline salts exhibit characteristics similar to those of the corresponding quinoline compounds (see this vol., i, 650). The following were prepared:

The action of aniline on uranyl nitrate yields *uranylaniline* or *phenyluranylamine*, $NPh\colon UO_2 + 6H_2O$, which crystallises also with $2H_2O$, and when heated with concentrated acetic acid gives a bright red solution and a precipitate of the black oxide, U_2O_5. The *sulphate*, $(NHPh)_2UO_2SO_4 + 3H_2O$; *acetate*, $(NHPh)_2UO_2(C_2H_3O_2)_2$, and *oxalate*, $(NHPh)_2UO_2C_2O_4 + 2H_2O$, were prepared. T. H. P.

2:3-Dihydroxybenzylmethylamine and 2:3-Dihydroxybenzyldimethylamine. RENÉ DOUETTEAU (*Bull. Soc. chim.*, 1912, [iv], 11, (13), 652—656. Compare Tiffeneau, Abstr., 1911, i, 972).—The starting point for the preparation of these substances was 2-hydroxy-3-methoxybenzaldehyde ("orthovanillin"), which can be methylated (compare Douetteau, Abstr., 1911, i, 973) to 2:3-dimethoxybenzaldehyde; by the action of alcoholic potassium hydroxide, this is converted into 2 : 3-*dimethoxybenzyl alcohol*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot OH,$$

(m. p. 48°, b. p. 257—258°/761 mm.), and 2 : 3-dimethoxybenzoic acid (m. p. 116°; methyl ester, m. p. 46·5°). The alcohol gives a *phenylurethane*, m. p. 94°, and an *acetate*, b. p. 158—160°/16 mm., 278—279°/754 mm., D^0 1·1621. The *chloride* of the alcohol could not be obtained in a higher degree of purity than 70% (b. p. 133—137°/13 mm., D^0 1·1958), but when heated with a benzene solution of methylamine in a sealed tube, it gave 2 : 3-*dimethoxybenzylmethylamine*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot NHMe,$$

b. p. 149°/19 mm., D^0 1·0699; *picrate*, m. p. 170°; *methiodide*, m. p. 181°. Attempts to prepare the *hydrochloride* of 2 : 3-*dihydroxybenzylamine* by demethylation yielded only a syrupy product.

2 : 3-*Dimethoxybenzyldimethylamine*, $C_6H_3(OMe)_2\cdot CH_2\cdot NMe_2$, was obtained by the action of dimethylamine on 2 : 3-dimethoxybenzyl chloride; it has b. p. 128—129°/14 mm., D^0 1·0461; *methiodide*, m. p. 179°. When heated with an equimolecular quantity of acetic anhydride, it undergoes scission into acetodimethylamide and 2 : 3-dimethoxybenzyl acetate (compare Tiffeneau, Abstr., 1911, i, 779). When heated with hydriodic acid at 130—140° it gives 2 : 3-*dihydroxybenzyldimethylamine*, $C_6H_3(OH)_2\cdot CH_2NMe_2$; *hydrochloride*, m. p. 165°.

The effect of the Grignard reagent on the two substituted benzaldehydes used in the course of the preceding work was investigated.

2-Hydroxy-3-methoxybenzaldehyde reacts with magnesium ethyl bromide with the formation of 2-hydroxy-3-methoxyphenyl-Δ^1-propylene, $OH\cdot C_6H_3(OMe)\cdot CH\colon CHMe$, m. p. 74—75°, b. p. 147—148°/16 mm. (compare Pauly, Abstr., 1911, i, 785). Magnesium ethyl iodide gives a mixture of this substance with *a*-2-*hydroxy*-3-*methoxyphenyl*-n-*propyl alcohol*, $OH\cdot C_6H_3(OMe)\cdot CHEt\cdot OH$, b. p. 165—170°/16 mm.

2 : 3-Dimethoxybenzaldehyde on treatment with magnesium ethyl bromide produces α-2 : 3-*dimethoxyphenyl*-n-*propyl alcohol*,

$$C_6H_3(OMe)_2\cdot CHEt\cdot OH,$$

a viscous liquid, b. p. 156—157°/14 mm., D^0 1·1212, which on distillation under ordinary pressure loses the elements of water with the formation of 2 : 3-*dimethoxyphenyl*-Δ^1-*propylene*,

$$C_6H_3(OMe)_2\cdot CH{:}CHMe,$$

b. p. 248—250°, D^0 1·0612. D. F. T.

Some Ethers of Cinnamyl Alcohol. HENRI BEAUFOUR (*Bull. Soc. chim.*, 1912, [iv], 11, 648—652).—A preliminary account of an investigation of the behaviour of various ethylenic substances towards treatment with iodine and yellow mercuric oxide.

Cinnamyl alcohol is converted into its sodium derivative by the action of sodamide, and then on careful treatment with methyl iodide, cinnamyl methyl ether, $CHPh{:}CH\cdot CH_2\cdot OMe$, is obtained, b. p. 227°, 117°/16 mm., D^0 1·0037 (compare Pschorr and Dickhauser, Abstr., 1911, i, 908). It gives a *dibromide*, m. p. 50·5°, and on treatment in ethereal solution with iodine and yellow mercuric oxide it gives the *iodohydrin*, $OH\cdot CHPh\cdot CHI\cdot CH_2\cdot OMe$, which can be converted into the corresponding *oxide*, and also be caused to undergo rearrangement into a branched aldehyde (compare Bougault, Abstr., 1902, i, 452). The action of iodine and mercuric oxide on the methyl and ethyl alcoholic solutions, however, yields the *methyl-iodohydrin* (b. p. 160—161°/15 mm.) and *ethyl-iodohydrin* (b. p. 164—165°/15 mm.) respectively.

Cinnamyl ethyl ether, $CHPh{:}CH\cdot CH_2\cdot OEt$, is obtained similarly to the methyl ether above; it is a colourless liquid, b. p. 238—239°/752 mm., 127—129°/17 mm. D^0 0·9938; *dibromide*, m. p. 72°.

D. F. T.

Unsaturated Compounds. II. Elimination of Hydrogen Chloride from Unsymmetrical Carbinyl Chlorides. ALEX. ORECHOFF and S. MEERSON (*Ber.*, 1912, 45, 1926—1930. Compare this vol., i, 436).—*Benzyl-β-phenylethylmethylcarbinol*,

$$CH_2Ph\cdot CH_2\cdot CMe(CH_2Ph)\cdot OH,$$

m. p. 50—51°, obtained in the usual manner from magnesium benzyl chloride and benzylacetone, is converted in ethereal solution by hydrogen chloride or hydrochloric acid, D 1·19, into the *chloride*, $C_{17}H_{19}Cl$, m. p. 61—62°. *Dibenzyl β-o-anisylethylcarbinol*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C(CH_2Ph)_2\cdot OH,$$

m. p. 72—73°, obtained in a similar manner from ethyl *o*-methoxydihydrocinnamate, forms a *chloride*, $C_{24}H_{25}OCl$, m. p. 90—91°. When boiled with pyridine, these two chlorides are converted into *αδ-diphenyl-β-methyl-Δ^{α}-butylene*, $CH_2Ph\cdot CH_2\cdot CMe{:}CHPh$, b. p. 205—206°/40 mm., and *α-phenyl-β-benzyl-δ-o-anisyl-Δ^{α}-butylene*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C(CH_2Ph){:}CHPh,$$

m. p. 56—57°, b. p. 266—267°/19 mm., respectively, the constitutions of the two hydrocarbons being proved by oxidation with ozone, whereby the former yields benzaldehyde and benzylacetone, whilst the

latter is converted into benzaldehyde and a ketone which probably has the formula $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2Ph$.

It is thus shown that, as in the case previously examined (*loc. cit.*), the nearest phenyl group has the strongest displacing influence on the hydrogen of the methylene group of the chloride. C. S.

Mechanism of the Grignard Reaction. ALEXANDER I. GORSKY (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 581—585).—The author discusses the work of von Baeyer and Villiger (Abstr., 1902, i, 355), Grignard (Abstr., 1903, i, 552), Schmidlin (Abstr., 1906, i, 392; 1907, i, 26), Tschitschibabin (Abstr., 1907, i, 1022), and Stadnikoff (Abstr., 1911, i, 435).

The reaction between triphenylmethyl ethyl ether, propyl iodide, and magnesium takes place most probably according to the equations: $CPh_3\cdot OEt + MgPrI = CPh_3I + Pr\cdot Mg\cdot OEt$ and $CPh_3I + MgPrI = MgI_2 + CHPh_3 + C_3H_6$. It is found that, under the conditions employed by Stadnikoff (*loc. cit.*), the reaction proceeds only in presence of alkyl iodide (perhaps also of bromide), whilst *iso*amyl chloride or iodobenzene does not react with magnesium and triphenylmethyl ethyl ether. This observation is explained by the fact that alkyl chlorides dissociate into alkylene and hydrogen chloride only with difficulty, and aromatic halogen derivatives exhibit no dissociation in this direction.

If, however, equimolecular proportions of *iso*amyl chloride and iodobenzene are taken together, the reaction proceeds energetically with formation of chlorobenzene and *iso*amyl iodide, the latter then dissociating into amylene and hydrogen iodide, and so giving the conditions for the reaction. The final products are the same as when propyl iodide is used, namely, triphenylmethane and the excess of triphenylmethyl ethyl ether does not take part in the reaction. The formation of amylene supports the scheme of the reaction given above.

With diphenylmethyl propyl ether and butyl iodide, the formation of tetraphenylethane probably results from the reactions: $CHPh_2\cdot OPr + C_4H_9\cdot MgI = CHPh_2I + C_4H_9\cdot Mg\cdot OPr$ and $2CHPh_2I + 2C_4H_9\cdot MgI = CHPh_2\cdot CHPh_2 + MgI_2 + 2C_4H_8$. T. H. P.

Ambrein. JOSEPH RIBAN (*Compt. rend.*, 1912, **154**, 1729—1732*).—Pelletier and Caventou in 1820 extracted from ambergris by means of alcohol a substance which they called ambrein. Having obtained a few grams of this substance accumulated in the course of years in a perfumery, the author has made a number of experiments in an attempt to elucidate its constitution.

Ambrein, $C_{23}H_{40}O$, purified by repeated crystallisations from alcohol is a white solid, separating in slender needles, m. p. 82°, which exhibit the phenomenon of superfusion for a long time even if sown with crystals. When warm and dry, it becomes highly electrified on slight rubbing. It has no optical activity, and is a neutral substance, insoluble in water, but soluble in most organic solvents, from which it does not crystallise out at all readily. When acted on by bromine in carbon tetrachloride solution, it gives an *octobromo*-derivative, $C_{23}H_{32}OBr_8$, a

* and *Bull. Soc. chim.*, 1912, [iv], **11**, 754—757.

white, vitreous solid. Chlorine under similar conditions decomposes it. On warming ambrein with phosphorus pentachloride, a white, amorphous mass of *pentachloroambrein*, $C_{23}H_{35}OCl_5$, is obtained. W. G.

Synthesis of Nitriles in the Cyclic Series. VICTOR GRIGNARD and E. BELLET (*Compt. rend.*, 1912, 155, 44—46).—Alkyl cyclic nitriles can be prepared by adding the corresponding magnesium alkyl bromide drop by drop to a cold ethereal solution of cyanogen, and subsequent hydrolysis. In this way the authors have prepared cyanohexamethylene [*cyclo*hexanecarboxylonitrile], b. p. 75—77°/16 mm. (compare Demjanoff, Abstr., 1904, i, 410), and o-, m-, and p-*methyl*cyclo*hexanecarboxylonitriles*, colourless liquids, having respectively b. p. 79—81°/16 mm., 86—87°/16 mm., 85—87°/18 mm. All these nitriles possess a strong, disagreeable odour, and are hydrolysed by alcoholic potassium hydroxide to the corresponding acid, without the formation of the intermediate amide. On reduction with sodium and alcohol, they yield the corresponding *methylhexahydrobenzylamines*, which are colourless liquids with a slightly fruity odour, of which the *meta*-compound has b. p. 114—116°/80 mm., and the *para*-, b. p. 113—115°/80 mm.

l-Pinene hydrochloride when slowly added to an ethereal solution of cyanogen gives d-*hydropinenecarboxylonitrile*, m. p. 157—158°, $\alpha_D + 1{\cdot}0°$ (compare Houben and Doescher, Abstr., 1911, i, 61). This nitrile on saponification yields the l-*acid*, $\begin{array}{l}CH_2{\cdot}CH\text{——}CH_2\\ |\qquad >CMe_2\quad |\\ CH_2{\cdot}CMe\text{——}CH{\cdot}CO_2H\end{array}$, m. p. 88—89°. W. G.

Synthesis of α-Phenyl-αβ-dimethylhydrocinnamic Acid [αβ-Diphenyl-α-methylbutyric Acid]. (Mme.) PAULINE RAMART-LUCAS (*Compt. rend.*, 1912, 155, 39—42).—An endeavour to elucidate the constitution of an acid, m. p. 173°, obtained on oxidising a hydrocarbon resulting from the dehydration of diphenyl-ψ-butylcarbinol (compare this vol., i, 449).

αβ-Diphenyl-α-methylbutyronitrile can be prepared from αβ-diphenylacrylonitrile by addition of magnesium methyl iodide followed by methyl iodide (compare Kohler, Abstr., 1906, i, 427), or by the action of sodamide followed by methyl iodide on αβ-diphenylbutyronitrile. The nitrile, so obtained, can be hydrolysed by heating with a mixture of hydrochloric and acetic acids in sealed tubes at 180°, giving *αβ-diphenyl-α-methylbutyric acid*, $CHMePh{\cdot}CMePh{\cdot}CO_2H$, m. p. 181—182°; thus the original acid is still unorientated. W. G.

Isomerism of Ethyl Formylphenylacetate. III. WILHELM WISLICENUS (*Annalen*, 1912, 389, 265—292. Compare Abstr., 1900, i, 9, 597).—Four modifications of ethyl formylphenylacetate are known: (i) the liquid α-form, which develops an intense bluish-violet coloration with ferric chloride, is simply related genetically to the metallic derivatives, and is undoubtedly the enolic modification,

$$OH{\cdot}CH{:}CPh{\cdot}CO_2Et;$$

(ii) β-modification, m. p. about 70°, which has hitherto been regarded as the aldo-form; (iii) Michael's modification, m. p. about 50° (Abstr.,

1906, i, 179), and (iv) γ-modification, m. p. about 100° (Wislicenus and Börner, Abstr., 1900, i, 597).

The author is of opinion that the α- and the γ-modifications are the only forms which are chemically individual; the other solid forms are mixtures of the α- and the γ-modifications.

The evidence on which this opinion is based is the following. The β-modification, m. p. about 70°, has been assumed to be the aldo-form, because it does not give a coloration with ferric chloride in dilute alcoholic solution. Against this view, however, is the fact that the β-modification is as easily soluble as the α in alkali hydroxides, and both solutions behave alike on acidification. A dilute methyl-alcoholic solution of the α-modification slowly, but almost entirely, loses its property of developing colour with ferric chloride, indicating the attainment of a state of equilibrium between the enolic and an aldo-modification. The same state is reached when the β-modification is kept in dilute methyl-alcoholic solution. The aldo-form in the solution, however, cannot be the β-modification, since the latter cannot be obtained directly from the solution either by evaporation or by precipitation with water. The true aldo-modification, $CHO \cdot CHPh \cdot CO_2Et$, of ethyl formylphenylacetate, therefore, has not been isolated; it exists only in dilute, alcoholic solution.

The γ-modification is obtained best by adding slowly a slightly alkaline 10% solution of the sodium derivative of ethyl formylphenylacetate to an excess of 25% sulphuric acid at 0°; it has m. p. 103—105°, which is raised to about 110° after keeping for some time. It has previously been regarded as a geometrical isomeride of the α-modification (*loc. cit.*). It is now shown to be the enol-aldo-form, $CHO \cdot CPh\dot{:}C(OH) \cdot OEt$, since it can under suitable conditions develop a transient, pure blue coloration with ferric chloride, restores the colour of decolorised magenta solution, and contains, by optical evidence, an ethylenic linking. The two remaining solid forms, Michael's and the β-modifications, are simply mixtures of the α- and the γ-modifications. This is proved as follows: It is known that the α-modification changes almost completely into the β by keeping. When a solution of ethyl sodioformylphenylacetate is acidified, the m. p. of the solid obtained varies between 50° and 105° according to the concentration of the hydrogen ions; the greater the concentration, the higher is the m. p. of the solid. Mixtures of the liquid α- and the solid γ-modifications yield solids of varying m. p. resembling the β- and Michael's modifications. Moreover, the lower is the m. p. of a solid mixture the greater is its solubility in petroleum, and the more intense is its colour reaction with ferric chloride. (The α-modification is easily soluble in petroleum, whilst the γ-modification is almost insoluble.) The α-modification when impure is unchanged by acids, but the quite pure substance is converted into solid mixtures of m. p. about 70—75°. Chloroform containing a little hydrogen chloride converts the solids of lower m. p. into the γ-modification; this in turn is converted slowly, but completely, into the α-modification in indifferent solvents.

The colour of decolorised magenta solution is restored by all the solid modifications; the α-modification does not do so except after long keeping (that is, after conversion into the β-form).

The metallic derivatives of ethyl formylphenylacetate are of the enol type. The copper derivative of the β-modification (Abstr., 1896, i, 552) is now shown to be the α-copper derivative mixed with basic copper sulphate and the β- or γ-modification of the ester.

Whilst the enolic constituent of a desmotropic combination can be detected by ferric chloride, the aldo-form can be identified by decolorised magenta solution. Also copper acetate or silver acetate can be used to detect the existence of aldo-enol equilibrium. By shaking a benzene solution of ethyl formylphenylacetate with aqueous copper acetate, the benzene acquires an intense green colour or remains colourless according as the solution contains much or little of the enolic form. Again, by shaking a methyl-alcoholic solution of the ester covered with benzene with ammoniacal silver nitrate, the deposition of black silver occurs first in the benzene layer and subsequently in the alcoholic liquid. C. S.

The Resolution of Racemic Cyanohydrins by means of an Optically Active Base. MARIO BETTI and JAN VAN GIFFEN (*Gazzetta*, 1912, **42**, i, 316—320).—β-Hydroxynaphthylbenzylamine reacts with cyanohydrins, thus: $C_{17}H_{15}ON + OH{\cdot}CHR{\cdot}CN = C_{17}H_{13}ON{:}CHR + H_2O + HCN$, and it is suggested that racemic cyanohydrins may be resolved by using the *d*-base.

Anisylidenecyanohydrin combines with the *d*-base, yielding a crystalline compound, $[\alpha]_D = +314°$. From the filtrate, a small quantity of lævorotatory cyanohydrin is obtained, together with a larger quantity of the inactive compound. Methylsalicylidenecyanohydrin behaves similarly, yielding a crystalline compound, $[\alpha]_D = +243°$, whilst only a small quantity of a lævorotatory product, yielding an inactive acid on saponification, is obtained from the filtrate. *o*-Nitrobenzylidenecyanohydrin reacts with the base, forming an insoluble compound of unknown constitution. C. H. D.

Dimorphism and Crystalline Form of Diphenylmaleic Anhydride. JULIEN DRUGMAN (*Zeitsch. Kryst. Min.*, 1912, **50**, 576—581).—Two modifications of this substance are described. The *α-modification* crystallises from acetone, etc., as large, pale greenish-yellow crystals with a slight bluish fluorescence, m. p. 155°, D^{15} 1·340; $a:b:c = 0{\cdot}5176:1:0{\cdot}7024$. The habit of the orthorhombic crystals varies widely according to whether they are grown from acetone or from toluene, whilst crystals grown from alcohol and from xylene are apparently hemimorphic. The *β-modification* crystallises, together with the α-modification, from acetone or from toluene in the presence of water. It forms small, almost colourless, monoclinic crystals with a strong blue fluorescence, m. p. 146°, D^{15} 1·345; $a:b:c = 2{\cdot}561(5):1:2{\cdot}327(5)$; $\beta = 101°33'$. The β-modification is a labile form; when heated, or when in contact with the α-modification, it passes over into the latter. L. J. S.

***o*- and *p*-Methoxybenzoylglyoxylic Esters.** ANDRÉ WAHL and M. DOLL (*Compt. rend.*, 1912, **155**, 49—51).—Ethylacetoacetate and its homologues are converted into $\alpha\beta$-diketonic esters by the action

of nitrous fumes. The authors are extending the reaction to the aromatic series.

Methyl *o*-methoxybenzoylacetate was not transformed into a diketonic ester by the above reaction, but yielded a white, crystalline *compound*, m. p. 141—142°, which was insoluble in the usual solvents, soluble in alkalis, but not reprecipitated by acids. Its analysis corresponds with methyl oximinomethoxybenzoylacetate, but it differs from it in its properties.

Methyl *p*-methoxybenzoylacetate when treated with nitrous fumes yields *methyl anisoylglyoxylate*, $OMe\cdot C_6H_4\cdot CO\cdot CO\cdot CO_2Me$, an orange-yellow, mobile liquid, b. p. 185—192°/10 mm., which reduces Fehling's solution and silver nitrate. It is insoluble in water, but combines with it giving a *hydrate*, colourless needles, m. p. 109—110°. It gives additive products with a number of reagents, and with others condenses normally. With hydroxylamine it yields a monoxime, m. p. 153—154°, identical with methyl oximinoanisoylacetate (compare Wahl and Silberzweig, *Compt. rend.*, 1910, 150, 538). With phenylhydrazine it yields a white *compound*,

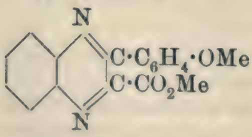
$$OMe\cdot C_6H_4\cdot CO\cdot C(NH\cdot NHPh)(OH)\cdot CO_2Me,$$

m. p. 193°, which on heating passes into the monophenylhydrazone, m. p. 121—122°, identical with methyl benzeneazoanisoylacetate (*loc. cit.*), and *phenylhydrazopyrazolone*, m. p. 177°.

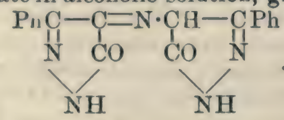
With *p*-nitrophenylhydrazine the product is either the *mono*-p-*nitrophenylhydrazone*, m. p. 175°, or p-*nitrophenylhydrazopyrazolone*, m. p. 340°, according to the temperature and proportion of the reagents used.

Hydrazine (1 mol.) in acetic acid solution gives a yellow, crystalline *compound*, m. p. 165°, and semicarbazide (1 mol.) gives a white, crystalline *compound*, m. p. 210°.

An *anilide*, m. p. 157—158°, and a *toluidide*, m. p. 152°, have been prepared from methyl anisoylglyoxylate. It condenses with *o*-phenylenediamine, giving a white, crystalline *compound* (annexed formula), m. p. 122°.



The authors have also prepared *methyl*, *propyl*, and iso*butyl benzoylglyoxylates*, which have respectively b. p. 146—149°/12 mm., 155—158°/12 mm., 161—164°/12 mm., and D_0^0 1·233, 1·159, 1·124. They are all yellow, mobile liquids, and will be dealt with further in a later paper. They react with hydrazine hydrate in alcoholic solution, giving 3:3'-*diphenylrubazonic acid*, m. p. 267°,



. W. G.

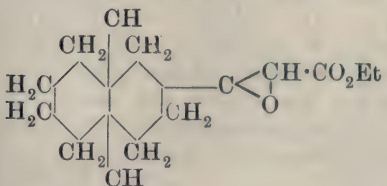
Angeli-Rimini Reaction [of Aldehydes]. Angelo Angeli (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 622—627).—The author replies to Balbiano's criticisms (this vol., i, 474) and gives the results of the application of the reaction to deoxybenzoin, piperylacetone, and benzyl methyl ketone.

Desoxylbenzoin yields benzhydroxamic acid, and piperylacetone, piperonalhydroxamic acid (compare Rimini, Abstr., 1901, i, 450).

With benzyl methyl ketone, a copper salt is obtained. which, on decomposition with dilute sulphuric acid, gives varying proportions of benzhydroxamic acid, acetylbenzylhydroxylamine, and a compound, m. p. 232°, containing sulphur and nitrogen. The second of these products is derived from acetylhydroxylamine isomeric with the hydroxamic acid which should be formed if the initial compound were an aldehyde instead of a ketone, and, like the hydroxamic acids, it is coloured red by ferric chloride; its copper salt is formed only when concentrated solution of acetylphenylhydroxylamine and copper acetate are employed, and, as only one hydrogen atom replaceable by metals is present, has the composition $(C_9H_{10}O_2N)_2Cu$.

This aldehyde reaction: (α) $R\cdot CHO + NH(OH)_2 = R\cdot C(OH){:}NOH + H_2O$, takes place in an alkaline medium, but excess of alkali may prevent the formation of hydroxamic acids. If the decomposition of dihydroxyammonia, according to the equation: (β) $2NH(OH)_2 = N_2O + 3H_2O$, is more rapid than the reaction (α), the hydroxamic acids will be obtained in small amount or not at all. But it is found that the reaction (α) may be activated by adding the calculated quantity of alkali in small portions and at wide intervals. If the concentrations of aldehyde and dihydroxyammonia (which is proportional to the alkali added) are indicated by C_a and C_b, the velocities of (α) and (β) are given by $dx/dt = K_1(C_a - x)(C_b - x)$ and $dx/dt = K_2(C_b - x)^2$, where K_1 and K_2 denote the respective velocity constants. The ratio of the velocities of (α) and (β) will be $K_1 . C_a . C_b / K_2 . C_b^2$ or KC_a/C_b, and this can be made greater than unity either by increasing C_a or by diminishing C_b. C_a cannot, however, be greatly increased, since concentrated solutions are already used, whereas C_b can always be made as small as desired, and reaction (β) hence rendered negligible. This conclusion is found to be confirmed experimentally, and it is only by such an artifice that salicylaldehyde and *m*-hydroxybenzaldehyde can be transformed into the corresponding hydroxamic acids. T. H. P.

Glycidic Esters of Decahydro-β-naphthyl Ketone, Decahydro-β-naphthaldehyde, and Methyldecahydro-β-naphthyl Ketone. GEORGES DARZENS and HENRI LEROUX (*Compt. rend.*, 1912, **154**, 1812—1814. Compare Abstr., 1905, i, 116, 601).—Decahydro-β-naphthyl ketone readily condenses with ethyl chloroacetate, giving the *glycidic* ester (annexed formula), a colourless, slightly viscous liquid, b. p. 148—150°/4 mm. It is readily saponified to the *acid*, a very viscous liquid, which on distillation under reduced pressure is decomposed, giving *decahydro-β-naphthaldehyde*, a colourless, mobile liquid, b. p. 95—96°/3 mm., which gives a *semicarbazone*, m. p. 178—179°.



Condensation of decahydro-β-naphthyl ketone with ethyl chloro-

propionate yields *ethyl decahydro-β-naphthylmethylglycidate*, a colourless, mobile liquid, b. p. 155—156°/4 mm. On saponification, it yields the *acid*, crystallising in fine needles, m. p. 149—150°. This acid is much less readily decomposed than its lower homologue, but on distillation it yields *decahydro-β-naphthyl methyl ketone*, a mobile liquid with a camphor-like odour, b. p. 94—95°/3 mm., which gives a *semicarbazone*, m. p. 240—241°. W. G.

A New Compound Occurring in Wood Vinegar (Methyl-*cyclo*pentenolone). JULIUS MEYERFELD (*Chem. Zeit.*, 1912, 36, 549—552).—Several alicyclic ketones are already known to exist in the products of distillation of wood.

*Methyl*cyclo*pentenolone*, $C_6H_8O_2$, is colourless, and has m. p. 106° and b. p. 210°, with slight decomposition. It crystallises well from organic solvents, and from hot water with H_2O. Its solution is slightly acid, and gives a violet coloration with ferric chloride. It reduces an alkaline solution of permanganate, yielding acetic and oxalic acids. It also reduces Fehling's solution and ammoniacal silver nitrate. It yields a monoacetyl derivative, and an osazone not containing oxygen, proving the presence of the group $-CO\cdot CH(OH)-$. On reduction, a mixture of the two 1-methyl*cyclo*pentanols, b. p. 146°, is obtained, whilst on removal of water a methyl*cyclo*pentene is obtained. The constitution has not been further determined, as six isomerides are possible.

The *osazone*, $C_{18}H_{18}N_4$, crystallises from alcohol, and has m. p. 140° (decomp.). The *acetyl* derivative forms colourless crystals, m. p. 65° and b. p. 129—130°/12 mm. The *phenylhydrazone* of the acetyl compound forms yellow needles, m. p. 170°. Hydroxylamine yields a *compound*, $C_6H_{10}O_2N_2$, probably containing the groups $\cdot NH\cdot OH$ and $:NOH$, as it forms a *diacetyl* derivative, m. p. 76°, exploding at 110°.

The ketone-alcohol forms metallic salts, of which the *zinc*,

$$(C_6H_7O_2)_2Zn,H_2O,$$

the *magnesium*, $(C_6H_7O_2)_2Mg,H_2O$, and *sodium*, $C_6H_7O_2Na$, salts have been analysed. C. H. D.

Action of Hydrazine on Ethylenic β-Substituted Amino-ketones. EMILE ANDRÉ (*Compt. rend.*, 1912, 155, 52—54).—Ethylenic β-substituted aminoketones of the types $NR^{II}R^{III}\cdot CR:CH\cdot COR^{I}$ and $NHR^{II}\cdot CR:CH\cdot COR^{I}$ readily condense with hydrazine with the elimination of the amines $NHR^{II}R^{III}$ or NH_2R^{II} and the formation of 3 : 5-disubstituted pyrazoles, which are also obtained by the same reaction from the corresponding acetylenic ketones or the ethylenic β-alkyloxy- or phenoxy-ketones (compare Moureu and Brachin, Abstr., 1903, i, 581 ; 1904, i, 824). The author has applied the reaction to dipropylaminoacetylstyrene, diethylaminopropionylstyrolene, *cyclo*hexylaminobutyrylstyrene, and diethylaminobenzoylstyrene. W. G.

Catalytic Hydrogenation of Benzylideneacetone [Styryl Methyl Ketone]. GUSTAVE VAVON (*Compt. rend.*, 1912, 154, 1705—1706).—Styryl methyl ketone, when dissolved in ether, is

readily reduced by hydrogen in the presence of platinum-black. By stopping the action at the required stages, three successive products can be obtained (compare Abstr., 1911, i, 657, 730).

a-Phenylbutan-γ-one, $CH_2Ph\cdot CH_2\cdot COMe$, the first product, is a colourless liquid, b. p. 110—112°/12 mm.; D_4^{17} 0·992; n_D^{17} 1·514. It gives an *oxime*, fine needles, m. p. 87°. The next stage in the reduction gives *a-phenylbutan-γ-ol*, $CH_2Ph\cdot CH_2\cdot CHMe\cdot OH$, a colourless liquid with a pleasant odour, b. p. 115—116°/12 mm.; D_4^{17} 0·976; n_D^{17} 1·513. It forms an *acetate*, b. p. 123—124°/13 mm.; D_4^{16} 0·991; n_D^{16} 1·489; and a *benzoate*, b. p. 195°/12 mm.; D_4^{15} 1·058; n_D^{15} 1·545.

The complete reduction of styryl methyl ketone gives *a*-cyclo*hexylbutan-γ-ol*, $C_6H_{11}\cdot[CH_2]_2\cdot CHMe\cdot OH$, a colourless liquid with an agreeable odour, b. p. 112°/14 mm.; D_4^{17} 0·905; n_D^{17} 1·467. It yields an *acetate*, b. p. 115—116°/12 mm.; D_4^{14} 0·932; n_D^{14} 1·450; and a *benzoate*, b. p. 190°/12 mm.; D_4^{14} 1·009; n_D^{14} 1·512. W. G.

Derivatives of Hexahydrobenzaldehyde. JULES FRÉZOULS (*Compt. rend.*, 1912, **154**, 1707—1708. Compare Abstr., 1910, i, 480).—Hexahydrobenzaldehyde does not condense with acetic anhydride or potassium cyanide, but under their influence, polymerises. On mixing it with acetophenone in the presence of sodium methoxide, immediate condensation takes place, giving *phenyl hexahydrostyryl ketone*, $C_6H_{11}\cdot CH\colon CH\cdot COPh$, colourless needles, m. p. 167—168°. By the condensation of benzaldehyde and hexahydroacetophenone, the isomeride cyclo*hexyl styryl ketone*, $CHPh\colon CH\cdot CO\cdot C_6H_{11}$, is obtained as large, colourless plates, m. p. 58—59°, which is readily acted upon by bromine in chloroform solution, giving the *dibromide*,

$$CHPhBr\cdot CHBr\cdot CO\cdot C_6H_{11},$$

long needles, m. p. 144—145°.

The yield of both the ketones is very poor indeed. An attempt to condense hexahydrobenzaldehyde and hexahydroacetophenone only gave an oily product which would not crystallise. W. G.

Catalytic Hydrogenation of Phenyl Styryl Ketone: Diphenylpropane and *sym*-Di*cyclo*hexylpropane. JULES FRÉZOULS (*Compt. rend.*, 1912, **155**, 42—44. Compare previous abstract).—An endeavour to prepare hexahydrobenzylidenehexahydroacetophenone, which was, however, unsuccessful, the ketone group being reduced prior to this stage.

If the vapour of phenyl styryl ketone is passed with hydrogen over freshly reduced nickel at 200°, *aγ-di*cyclo*hexylpropane*,

$$C_6H_{11}\cdot[CH_2]_3\cdot C_6H_{11},$$

is produced as a colourless liquid, b. p. 291—292° (corr.); D_{24}^{24} 0·8752; n_D^{24} 1·4736. It solidifies at −30° to fine needles, m. p. −17°.

Under similar conditions, but using nickel that has already served for several days, the product is *aγ*-diphenylpropane,

$$CH_2Ph\cdot CH_2\cdot CH_2Ph,$$

a colourless liquid, b. p. 299—300° (corr.); D_{19}^{19} 0·9018; n_D^{19} 1·5028 (compare Claus and Mercklin, Abstr., 1886, 143). W. G.

Iodoketones and their Derivatives with Uni- and with Multi-valent Iodine. CONRAD WILLGERODT and KARL BURKHARD (*Annalen*, 1912, **389**, 292—305).—*o*-Iodoanisole, acetyl chloride, and aluminium chloride react in carbon disulphide cooled by a freezing mixture to form, ultimately, o-*iodoanisyl methyl ketone*,

$$OMe{\cdot}C_6H_3I{\cdot}COMe,$$

m. p. 103°, white needles. From this, *anisyl methyl ketone* o-*iododichloride*, $OMe{\cdot}C_6H_3Ac{\cdot}ICl_2$, decomp. 128°, yellow leaflets, is obtained in the usual manner; the iodoso- and the iodoxy-compounds cannot be prepared. 5-*Acetyl-2-methoxydiphenyliodinium chloride*,

$$OMe{\cdot}C_6H_3Ac{\cdot}IPh{\cdot}Cl,$$

m. p. 198°, white leaflets, obtained by treating the preceding iododichloride and mercury diphenyl with water, yields an alkaline solution of the *iodinium hydroxide* with silver oxide and water, and the following salts by double decomposition: *bromide*, m. p. 190°; *iodide*, m. p. 169° (*periodide*, $C_{15}H_{14}O_2I_4$, m. p. 115°, garnet-red crystals); *dichromate*, decomp. 151°, yellow needles, and *platinichloride*, m. p. 161°.

o-*Iodoanisyl chloromethyl ketone*, $OMe{\cdot}C_6H_3I{\cdot}CO{\cdot}CH_2Cl$, m. p. 134°, obtained by the action of chlorine on a not too strongly cooled solution of *o*-iodoanisyl methyl ketone in chloroform, yields *o*-iodo-*p*-anisic acid by oxidation with potassium permanganate, and the *iododichloride*, $CH_2Cl{\cdot}CO{\cdot}C_6H_3(OMe){\cdot}ICl_2$, yellow leaflets, by passing chlorine into its cooled solution in a little chloroform.

By methods similar to the preceding, o-*iodophenetyl methyl ketone*, $OEt{\cdot}C_6H_3I{\cdot}COMe$, m. p. 81°, and the following derivatives have been prepared: *phenetyl methyl ketone* o-*iododichloride*, decomp. 103°; 5-*acetyl-2-ethoxydiphenyliodinium chloride*, m. p. 192°, and the corresponding *platinichloride*, decomp. 172°; *bromide*, m. p. 191°; *iodide*, m. p. 164°; *periodide*, decomp. 125°, and *dichromate*, m. p. 157° (decomp.).

The reaction between *o*-iodoanisole and benzoyl chloride in cold carbon disulphide with aluminium chloride leads to the formation of 3-*iodo*-4-*methoxybenzophenone*, $OMe{\cdot}C_6H_3I{\cdot}COPh$, m. p. 80°, from which the following have been prepared: 4-*methoxybenzophenone* 3-*iododichloride*, decomp. 123°; 3-*iodoso*-4-*methoxybenzophenone*, decomp. 108° (*acetate*, decomp. 163°); 3-*iodoxy*-4-*methoxybenzophenone*, decomp. 190°, and 5-*benzoyl*-2-*methoxydiphenyliodinium chloride*, $OMe{\cdot}C_6H_3Bz{\cdot}IPh{\cdot}Cl$, m. p. 181°, and its corresponding *platinichloride*, decomp. 194°, *bromide*, m. p. 179°, *iodide*, m. p. 156°, and *dichromate*, decomp. 167°.

C. S.

Action of Phosphorus Tribromide and Phosphorus on β-Benzopinacolin. P. J. MONTAGNE (*Chem. Weekblad*, 1912, **9**, 468—470. Compare Stoermer, Abstr., 1904, i, 181; Stoermer and Martinsen, Abstr., 1907, i, 446).—Stoermer's work on the interaction of phosphorus tribromide and phosphorus with compounds containing the carbonyl group renders it probable that β-benzopinacolin would yield tetraphenylethylene according to the scheme:

$$CPh_3{\cdot}COPh \longrightarrow [CPh_3{\cdot}\overset{\wedge}{CPh}] \longrightarrow CPh_2{:}CPh_2.$$

At 200—210° there is no action; at 240—250°, triphenylmethane (m. p. 93·5°) is formed, the necessary hydrogen being derived from

decomposition of part of the molecule. A small proportion of anthracene is also formed. A. J. W.

Number of Isomerides of Merotropic and Desmotropic Compounds. ARTHUR MICHAEL (*Annalen*, 1912, 390, 30—46).—Previously it has been shown (Abstr., 1906, i, 179) that the three forms of ethyl formylphenylacetate are enolic, the two forms of oxalacetic acid are ketonic, and that dibenzoylacetylmethane exists in one enolic and two ketonic modifications. Now it is shown (following abstracts) that dibenzoylpropionylmethane also exists in two ketonic modifications. Contrary to the expectation that these two forms would resemble closely the two ketonic forms of dibenzoylacetylmethane, it has been found that the presence of the propionyl in place of the acetyl group materially alters the ease of the keto-enolic transformation.

The existence of the preceding two dibenzoylacylmethanes, each in two ketonic modifications, is specially important in that it shows that the structures of such modifications cannot be those corresponding with racemic and with meso-configurations, as has previously been assumed in the case of alkyl diacylsuccinates and other substances which contain two equally asymmetric carbon atoms and exist in two ketonic modifications.

The cause of the preceding cases of isomerism undoubtedly is to be found in the spatial arrangement of the atoms in the molecule. A conception of stereochemical formulæ is given, based on the law of entropy and bearing special reference to the possible number of isomerides, as conditioned by the free and the bound chemical energies of the atoms.

Not only the structural formula, but also the stability, of an organic compound is determined by these factors. If it is assumed that the bound energy of two singly linked carbon atoms is insufficient to prevent rotation, then for a certain configuration the maximum entropy of the system will be attained, or, in other words, the free chemical energy of atoms which are not directly united wlll be as fully as possible transformed into bound energy and heat. When this favoured configuration has been attained, oscillatory motion may occur, but not free rotation, because this would necessitate a spontaneous transformation of bound into free chemical energy, that is, a degradation of the entropy. The fact that a saturated organic compound, which theoretically can exist in several different modifications, actually occurs only in one or in stereoisomeric forms, must depend on the change of entropy accompanying the conversion of one form into another. If the change is considerable, only one form is stable ; if it is relatively small, several forms may exist ; whilst if the change is small enough, the several forms are interconvertible by very feeble physical or chemical agencies. C. S.

Isomeric Ketonic Modifications of Dibenzoylacetylmethane. ARTHUR MICHAEL (*Annalen*, 1912, 390, 46—48).—The known ketonic modification, the β-form, of dibenzoylacetylmethane, is converted by boiling for one-half to three-quarters of an hour with acetyl chloride into

a new ketonic modification, *γ-dibenzoylacetylmethane*, m. p. 146—149°, which is unimolecular, does not develop a coloration with alcoholic ferric chloride except after some time, and can be crystallised only from acetyl chloride without undergoing a partial change into one of the other modifications. The m. p. depends largely on the duration of the heating, since the γ-form changes by heating into the β-ketonic and the enolic modifications.

Comparative experiments on the behaviour of the β- and the γ-modifications in various solvents, such as acetyl chloride, acetic anhydride, methyl iodide, carbon tetrachloride, ethylene dibromide, etc., show that usually the γ- changes to the β-form, and that enolisation does not occur to any great extent, as a rule; in chloroform, however, the γ-modification is almost completely, the β-modification to the extent of one-third, changed to the enolic form. In benzene solution, in the presence of 1% aqueous sodium carbonate, the β-form is enolised thrice as rapidly as the γ-form. C. S.

Isomeric Ketonic Modifications of Dibenzoylpropionylmethane. ARTHUR MICHAEL and HAROLD HIBBERT (*Annalen*, 1912, **390**, 68—88).—The reaction between benzoylpropionylmethane and anhydrous sodium carbonate and benzoyl chloride in ether in the presence of two to three drops of water leads to the formation of the enolic modification of dibenzoylpropionylmethane, $C_{18}H_{16}O_3$, a heavy, viscous liquid, which develops a deep red coloration with alcoholic ferric chloride, easily changes to the β-ketonic modification, and dissolves readily and completely in aqueous sodium carbonate. The ketonisation of the enolic modification is greatly retarded by certain solvents, particularly chloroform.

The β-ketonic modification, m. p. 122—123°, is obtained by keeping the liquid form for five days and washing the resulting solid with petroleum to remove traces of the unchanged enolic modification. It crystallises unchanged, in prisms or needles, from glacial acetic acid, but is enolised by other solvents. It dissolves slowly in aqueous sodium carbonate, and develops a coloration with ferric chloride only after about thirty seconds, both reactions being preceded by enolisation. Unlike β-dibenzoylacetylmethane, β-dibenzoylpropionylmethane is enolised by acetyl chloride, not converted directly into the γ-ketonic modification. However, it crystallises from hot 50% alcohol as a mixture, m. p. 125—133°, which, after being heated at 100—102° for two to three hours, is converted by boiling acetyl chloride into the γ-ketonic form, m. p. 151—153°. *γ-Dibenzoylpropionylmethane*, like the β-form, is unimolecular, and behaves in a similar manner towards aqueous sodium carbonate and towards alcoholic ferric chloride. In most solvents it changes to the β-form or to a mixture of the β- and the γ-forms; from glacial acetic acid, dichoroethylene, or chloroform, however, it can be recovered almost unchanged.

The β- and the γ-forms behave alike towards fatty tertiary amines (compare Michael and Smith, Abstr., 1908, i, 943). C. S.

Constitution of Natural Chrysazin Derivatives. OTTO A. OESTERLE (*Arch. Pharm.*, 1912 **250**, 301—306).—Chrysophanic acid,

aloe-emodin, and rhein are anthraquinone derivatives, each containing a side-chain in the β-position, but whether this position is 2 or 3 is still an open question. Fischer, Falco, and Gross regard the side-chains are being in position 3 (Abstr., 1911, i, 309). The author at one time believed them to be in position 2, but since rhein is converted through its amide and amine into a trihydroxyanthraquinone which is not identical with 1 : 2 : 8-trihydroxyanthraquinone, he is now of opinion that the carboxyl group in rhein occupies position 3 and consequently the side-chains in chrysophanic acid and in aloe-emodin also occupy the same position.

The 1 : 3 : 8-*trihydroxyanthraquinone* obtained from rhein has m. p. 277—278°, forms an *acetate*, m. p. 197—198°, dissolves in dilute alkalis with a violet-red colour, and develops an orange coloration in concentrated sulphuric acid. C. S.

Oxidation of Unsaturated Compounds with Organic Peroxides. III. Oxidation of Derivatives of Unsaturated Compounds with Two Double Linkings. NIKOLAUS PRILESCHAEFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 613—647. Compare Abstr., 1911, i, 604).—The present paper deals with the oxidation, by means of benzoylhydroperoxide, of compounds containing two double linkings. In these cases the reaction proceeds in the normal way, and, in dependence on the proportion of active oxygen employed, either one or both of the double linkings may be oxidised, the less hydrogenated of the two linkings being oxidised first.

The velocity of the reaction and the properties of the oxide obtained depend, not only on the distribution of the oxygen groups with reference to the double linkings, but also on their character—whether aldehydic, alcoholic, etc. In the case of unsaturated alcohols, if the oxygen ring is in the $\alpha\beta$-position as regards the hydroxyl group, it exhibits considerable stability and inertness, being incapable of hydration. In compounds containing either an esterified alcohol group, such as acetyl-linalool, or a carboxyl group, oxidation of an $\alpha\beta$-double linking is so slow that it may be regarded as virtually absent. When aldehydes and ketones with conjugated systems of double linkings are oxidised, the oxide formed is so unstable that it undergoes decomposition with formation of an aldehyde with a carbon atom chain containing one less member than that of the original compound. With keto-oxides, the decomposition occurs at the double linking and yields two aldehyde molecules.

Geraniol monoxide, $CMe_2{<}\genfrac{}{}{0pt}{}{CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH_2\cdot OH}{O}$, obtained by employing 1 atom of active oxygen per mol. of the alcohol, is a colourless, viscous liquid, b. p. 157—158°/25 mm., D_0^0 0·9716, D_{16}^{16} 0·9610 n_D^{16} 1·4681. In presence of traces of acid, it combines energetically with water, giving the *trihydric alcohol*, $C_{10}H_{17}(OH)_3$, which is a faintly yellow, viscous liquid, b. p. 204—206°/19 mm., D_0^0 1·0606, D_{16}^{16} 1·0486, n_D^{16} 1·4935, and yields a *triacetyl* derivative, $C_{10}H_{17}O_3Ac_3$, b. p. 208°/25 mm., D_0^0 1·0756, D_{16}^{16} 1·0619 (compare Markownikoff and Reformatsky, Abstr., 1893, i, 662; Wagner, *Proc. Warsaw Soc. Nat.*, 1896). The oxidation of one ethylene linking of

geraniol by the hydroperoxide is accompanied by attack of the hydroxyl group, a small proportion being obtained of a compound, b. p. 119—120°/25 mm., having aldehydic properties; the products of the reaction contain also a higher fraction, consisting of a mixture of the dioxide (see below) with condensation products.

Geraniol dioxide, $\begin{matrix}CMe_2\\ | \\ O\text{——}\end{matrix}\!\!>CH\cdot CH_2\cdot CH_2\cdot CMe<\!\!\begin{matrix}CH\cdot CH_2\cdot OH\\ | \\ O\end{matrix}$, obtained by employing 2 atoms of active oxygen per mol. of geraniol, is a colourless, mobile liquid, b. p. 180—183°/25 mm., D_0^0 1·0587, D_{16}^{16} 1·0472, n_D^{16} 1·4653, and on hydration gives two isomeric, crystalline *trihydric oxyalcohols*:

$$(1)\ OH\cdot CMe_2\cdot CH(OH)\cdot[CH_2]_2\cdot CMe<\!\!\begin{matrix}CH\cdot CH_2\cdot OH,\\ | \\ O\end{matrix}$$

monoclinic prisms, m. p. 145—146°; the *triacetyl* derivative,

$$C_{10}H_{17}O(OAc)_3,$$

is a colourless, viscous liquid, b. p. 189·5—190°/14 mm., D_0^0 1·1396, D_{16}^{16} 1·1253; (2) m. p. 163—164°. These two isomerides are optically inactive and are hence derived from the limonene and terpinolene forms of geraniol; they are accompanied by an isomeric liquid product, which is probably a mixture of the two crystalline compounds, but no pentahydric alcohol could be isolated (compare Wagner, *loc. cit.*).

Linalool monoxide, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH<\!\!\begin{matrix}CH_2\\ | \\ O\end{matrix}$, is a colourless, mobile liquid, b.p. 197—198°/758 mm., D_0^0 0·9660, D_{16}^{16} 0·9520, n_D^{16} 1·45567, $[\alpha]_D$ −5°, and forms an *acetyl* derivative, $C_{10}H_{17}O_2Ac$, b. p. 118—119°/25 mm., D_0^0 0·9901, D_{16}^{16} 0·9770, n_D^{16} 1·44972, $[\alpha]_D$ −4·83°, which does not undergo hydration in presence of acid. Attempts to hydrate the monoxide were unsuccessful, the reaction being accompanied by condensation and, apparently, dehydration; the resulting product is an *aldehyde*, $C_{10}H_{16}O$, b. p. 120—122°/25 mm., D_0^0 0·8706, D_{16}^{16} 0·8576, n_D^{16} 1·5038.

Linalool dioxide, $\begin{matrix}CMe_2\\ | \\ O\text{——}\end{matrix}\!\!>CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH<\!\!\begin{matrix}CH_2\\ | \\ O\end{matrix}$, is a colourless liquid, b. p. 131—133°/25 mm., D_0^0 1·0552, D_4^{16} 1·0140, n_D^{16} 1·46170, $[\alpha]_D$ +5·3°. On hydration it yields the *trihydric oxyalcohol*, $OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH<\!\!\begin{matrix}CH_2\\ | \\ O\end{matrix}$, as a viscous liquid, b. p. 207—212°/26 mm.; with acetic anhydride, this compound yields the *tetra-acetyl* derivative, $C_{10}H_{17}(OH)(OAc)_4$, b. p. 207—209°/20 mm., D_0^0 1·1249, D_{16}^{16} 1·1114, n_D^{16} 1·4531.

Acetyl-linalool monoxide, $\begin{matrix}CMe_2\\ | \\ O\text{——}\end{matrix}\!\!>CH\cdot CH_2\cdot CH_2\cdot CMe(OAc)\cdot CH{:}CH_2$, is a colourless, mobile liquid, b. p. 138—139°/25 mm., D_0^0 0·9879, D_4^{16} 0·9742, $n_D^{16\cdot 1}$ 1·44847, $[\alpha]_D$ −2·58°. On hydration, it gives a mixture of the *trihydric alcohol*, $C_{10}H_{17}(OH)_3$, and its monoacetyl derivative, $C_{10}H_{17}(OH)_2\cdot OAc$; the latter could not be isolated, but the former is a colourless, viscous liquid, b. p. 177—180°/15 mm., which gradually deposits crystals, m. p. 54—55°.

Acetyl-linalool dioxide could not be obtained, benzoylhydroperoxide oxidising the double linking in the $\alpha\beta$-position to the acetyl group only with great difficulty.

Citral monoxide, $\left.\begin{array}{l}CMe_2\\ \mid\\ O\end{array}\right>CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CHO$, is a mobile liquid which rapidly turns yellow in the air, b. p. 144·5—145·5°/20 mm., D_4^{16} 0·9679, n_D^{16} 1·47848; it gives all the reactions of aldehydes, its oxime and semicarbazone being non-crystalline. With water it gives the *glycol*, $OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CHO$, which is a mobile liquid, b. p. 141—142°/24 mm., D_0^0 1·0584, D_{16}^{16} 1·0335, and forms a non-crystalline oxime and semicarbazone. Oxidation of the glycol with moist silver oxide yields the unsaturated *acid*,

$$OH\cdot C_9H_{14}\cdot CO_2H,$$

b. p. 176—180°/19 mm., which could not be obtained quite pure. When heated in a sealed tube with active anhydride, the glycol reacts in the enolic form (compare Semmler and Schossberger, Abstr., 1911, i, 475), giving the *triacetyl* derivative,

$$OAc\cdot CMe_2\cdot CH(OAc)\cdot CH_2\cdot CH_2\cdot CMe{:}C{:}CH\cdot OAc,$$

b. p. 205—207°/15 mm.

In the preparation of citral dioxide, the latter decomposes, yielding formic acid and the volatile *aldehydic oxide*,

$$\left.\begin{array}{l}CMe_2\\ \mid\\ O\end{array}\right>CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CHO,$$

b. p. 114—115°/25 mm., D_0^0 0·9724, D_4^{16} 0·9419, n_D^{16} 1·43728, which gives a non-crystalline oxime and semicarbazone. This compound is readily hydrated to the *aldehydic glycol*, $C_9H_{16}O(OH)_2$, b. p. 161—162°/25 mm., D_0^0 1·0690, D_{16}^{16} 1·0573, n_D^{16} 1·4710.

Benzylideneacetone oxide, $\left.\begin{array}{l}CHPh\\ \mid\\ O\end{array}\right>CHAc$, is a mobile, golden-yellow liquid, b. p. 123—125°/11 mm., D_0^0 1·0835, D_{16}^{16} 1·0694, which, in presence of water, undergoes gradual decomposition into benzaldehyde and probably methylglyoxal; the same decomposition occurs on keeping or distilling the oxide.

With increase of the number of oxygen atoms united to the carbon in the $\alpha\beta$-position with respect to the double linking, oxidation by means of benzoylhydroperoxide no longer occurs. Attempts to oxidise cinnamic acid in this way were unsuccessful. T. H. P.

The Isomeric Tanacetyl Alcohols. VINCENZO PAOLINI and BIANCA DIVIZIA (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 570—574).—It has been shown (Paolini, Abstr., 1911, i, 730) that tanacetyl alcohol (thujol) is a mixture of two isomerides. A dextrorotatory tanacetone, distinct from β-tanacetone, has now been isolated from thuja oil, and yields on reduction a mixture of alcohols quite similar to the ordinary tanacetyl alcohol, in which β-thujyl alcohol predominates. Similarly, a mixture has been isolated from the products of reduction of oil of absinthe, the fraction of b. p. 208—210° being used. From this, a phthalate with $[\alpha]_D$ +2°28′ and m. p. 95—96° has been obtained, yielding on hydrolysis the alcohol, with $[\alpha]_D$ +50°01′. It is proposed

to term this alcohol *δ-thujyl alcohol*, reserving γ for the alcohol accompanying it in oil of absinthe. C. H. D.

The Density of Camphor as Deduced from the Densities of its Solutions in Different Solvents. H. MALOSSE (*Compt. rend.*, 1912, **154**, 1697—1698).—The densities at 20° of solutions of camphor in the following solvents have been determined: 99% alcohol, 90% alcohol, acetone, methyl alcohol, benzene, ethyl acetate, olive oil, dimethylaniline, acetic acid, and carbon tetrachloride; the concentrations of the solutions varied from 10 to 60 grams of camphor per 100 grams of solution. Graphs of the results were then drawn, and extrapolated to a solution containing 100 grams of camphor, that is, pure camphor. The mean density thus obtained is 0·963, the greatest deviations from the mean being $\pm$0·002. T. S. P.

Essential Oils. IV. Essence of Mespilodaphne pretiosa. GUSTAVE LALOUE (*Bull. Soc. chim.*, 1912, [iv], **11**, 602—606. Compare Abstr., 1911, i, 138).—The author has studied the essential oils obtainable from the branches and wood of the *Mespilodaphne pretiosa*, belonging to the Lauracea family. The branches on distillation with steam yield 0·5% of a very mobile, pale yellow oil, D_4^{15} 0·8912; α_D 7°20′; n_D^{20} 1·469; acid number, 1·4; acetyl number, 165·2. It has a smell closely resembling that of linalool, and is chiefly composed of that alcohol. The wood on similar treatment yields a mixture of a light and a heavy oil, the total yield being 0·69%. The lighter oil, which constitutes five-sevenths of the mixture, is greenish-yellow, with an odour of rosewood. Its constants are: D_4^{15} 0·9539; α_D + 8°48′; n_D^{20} 1·501; acid number, 0·7; saponification number, 100·8; acetyl number, 205·1. The heavy fraction is a light brown oil with an odour of cinnamon, D_4^{15} 1·0551; α_D + 3°8′; n_D^{20} 1·545; acid number, 3·5; saponification number, 203·7; acetyl number, 247·8. It consists, for the greater part, of a benzoate, which is probably that of linalool or geraniol. W. G.

Constituents of Oil of Savin. J. WATSON AGNEW and ROBIN B. CROAD (*Analyst*, 1912 **37**, 295—298).—The oil was first hydrolysed with potassium hydroxide, then distilled with steam, and the distillate, after being dried over anhydrous sodium sulphate, submitted to fractional distillation. The following yields were obtained: First runnings (pinene), b. p. 150—160°, 1·7%; sabinene, b. p. 162—166°, 16·0%; terpinene fraction, b. p. 175—185°, 5·3%; sabinol, b. p. 208—209°, 17·0%; residue, b. p. above 210°, 16·0%; resin from steam-distillation, 31·0%; acids (acetic, formic, and another acid, m. p. 85°), 7·0%. Certain samples examined yielded large quantities of pinene, and had evidently been mixed with oil of turpentine. W. P. S.

Production and Polymerisation of Butadiene, Isoprene, and their Homologues. WILLIAM H. PERKIN (*J. Soc. Chem. Ind.*, 1912, **31**, 616—624).—Despite frequently recurring statements to the contrary, there can now be no doubt that caoutchouc may actually be obtained synthetically by the polymerisation of isoprene and its homologues, and that the synthetic product is really caoutchouc and strictly comparable with natural caoutchoucs.

The raw material for the synthetic production of caoutchouc must be available in large quantities, and the only materials fulfilling the necessary conditions seem to be wood, starch, sugar, petroleum, and coal.

Much work has been done on the halogenation of hydrocarbons, such as pentane and *iso*pentane and the elimination of halogen hydride from the products, and the conversion of lactic acid into dimethylallene and isoprene by a somewhat complicated process has been investigated, but the important method whereby isoprene may be obtained readily and in quantity requires *iso*amyl alcohol as the initial material. *iso*Amyl chloride, obtained by the action of hydrogen chloride on the fraction, b. p. 128—131°, of commercial fusel oil, is chlorinated in the vaporous state in sunlight or the light of a mercury lamp, in a specially constructed apparatus, whereby the formation of more highly halogenated substances than dichlorides is prevented. The chlorinated product can be separated by careful fractionation into $\gamma\delta$-dichloro-β-methylbutane, b. p. 142°, $\beta\delta$-dichloro-β-methylbutane, b. p. 152—155°, and *$\alpha\delta$-dichloro-β-methylbutane*, b. p. 170—172°, the constitution of the last being proved by its conversion ultimately into β-methyladipic acid. All three dichlorides yield isoprene when passed over hot soda-lime, so that in the preparation of the hydrocarbon the fraction, b. p. 140—180°, of the chlorinated products is passed directly over soda-lime in an iron tube at about 470°; the yield of isoprene is about 40% of that theoretically possible.

The polymerisation of isoprene to caoutchouc is effected by Matthews' sodium process, which has the important advantages over other methods that it is practically quantitative, can be performed in the cold or at a very moderate heat, and is not seriously affected by the presence of impurities, such as β-methyl-Δ^{β}-butylene or other hydrocarbons which are not capable of polymerisation to caoutchouc. The isoprene is sealed up with about 3% of thin sodium wire, and is heated at about 60° for several days; the dark brown product may be treated with acetone, and the precipitated caoutchouc may be washed with alcohol or heated with steam to remove acetone and any unpolymerised hydrocarbon.

There is every reason to believe that this process may be developed into an actual process for the manufacture of rubber provided that some cheap means of obtaining fusel oil in quantity is discovered.

Reference is made to Fernbach's fermentative processes, whereby starch is converted into acetone, on the one hand, and fusel oil on the other. The fusel oil thus produced contains a high percentage of butyl alcohol. Since Harries has shown that the rubber obtained by the polymerisation of $\Delta^{\alpha\gamma}$-butadiene is of better quality than that obtained from isoprene (Abstr., 1911, i, 798), butyl alcohol has been converted into butyl chloride, and this, by chlorination in the apparatus previously mentioned, into a mixture of $\alpha\beta$-, $\alpha\gamma$-, and $\alpha\delta$-dichlorobutanes. All of these yield $\Delta^{\alpha\gamma}$-butadiene when passed over hot soda-lime.

$\alpha\gamma$-Dichlorobutane has also been obtained by the following method. Acetaldehyde is converted by very dilute potassium carbonate into aldol, which is then reduced, electrolytically or by neutral reducing

agents, to $\alpha\gamma$-butylene glycol; the latter is converted by hydrochloric acid into $\alpha\gamma$-dichlorobutane, from which the butadiene is produced by the soda-lime method. The butadiene is polymerised to butadiene rubber by the sodium process. The author does not go so far as to say that synthetic rubber is identical with natural caoutchouc, but states that it is comparable with ordinary caoutchouc in that it can be vulcanised and answers all the other tests to which caoutchouc must be put by the manufacturer. C. S.

Chemistry of Caoutchouc. IV. DAVID SPENCE (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 299—306).—The effect of temperature on the vulcanisation of caoutchouc has been investigated. Practically no vulcanisation takes place in good specimens heated to 40°; the change is not appreciably accelerated on exposure to sunlight. On the other hand, partly decomposed caoutchouc undergoes considerable vulcanisation under the same conditions. Even at temperatures just below 60°, vulcanisation is very slow; above that temperature it is much more rapid. The widely accepted view that it is impossible to vulcanise caoutchouc so that all the free sulphur disappears is erroneous. G. S.

Occurrence and Method of Formation of Resin-Acids. II. JOHN KÖHLER (*J. pr. Chem.*, 1912, 85, [ii], 523—534. Compare Abstr., 1906, i, 100).—It has been shown previously that a white, crystalline resin, consisting essentially of sapinic acids, is occasionally found in winter under the bark of Swedish pines and firs. This particular variety of resin (winter-resin) is also met with during other seasons, but then invariably contains turpentine. The more frequent occurrence of this resin in winter is referred to the sensitiveness of the sapinic acids towards heat and atmospheric oxygen.

Whilst making observations on the occurrence of winter-resin in the neighbourhood of Wengen in the Bernese Oberland, the author came across two instances in which the winter-resin (of red firs) was associated with a pale yellow liquid, which is considered to be the parent substance of the resin acids.

The liquid is acid in character and rapidly becomes partly crystalline, owing to transformation into resin acids, but whether this change is due to atmospheric oxidation could not be determined. From experiments on the molecular weight of the liquid in glacial acetic acid before and after transformation, and allowing for the resin acids and turpentine present in the liquid, the molecular weight of the substance is estimated at 154.

The author inclines to the view that the parent substance consists of an aldehyde or camphor-like compound, $C_{10}H_{16}O$, from which the resin acids are formed by oxidation as follows: $2C_9H_{15}\cdot CHO + O = C_{19}H_{29}\cdot CO_2H + H_2O$.

The crystalline resin associated with the above-mentioned liquid contained in one instance 25% of *l*-pimaric acid, whilst the crystalline substance deposited from the liquid itself consisted almost entirely of sapinic acids. In the other case the resin was composed of almost pure *l*-pimaric acid. F. B.

Chemical Examination of Pine-resin (from Picea excelsa). III. John Köhler (*J. pr. Chem.*, 1912, 85, [ii], 534—564).—The author finds that *l*-pimaric acid, which, hitherto, has been isolated only in an impure condition from galipot, is a common constituent of the resin of the red fir (*Picea excelsa*).

It is occasionally found in fairly well-developed crystals in the winter-resin obtained from the upper portion of the stem, but is generally accompanied by more readily soluble acids (probably sapinic acids) of a less rotatory power. It has the formula $C_{20}H_{30}O_2$ and $[\alpha]_D^{20}$ $-280{\cdot}5°$. The m. p. is indefinite (134—152°), owing to partial transformation into colophonic acids.

When heated, it yields a mixture of *l*-colophonic acids, identical with the *α*-colophonic acids obtained from sapinic acid, together with *i*-colophonic acid.

The active colophonic acids crystallise in the monoclinic system, and cannot be separated by fractional crystallisation.

i-Colophonic acid crystallises in prisms belonging to the rhombic system: $[a:b:c = 0{\cdot}47698:1:\quad c]$.

The colophonic acids are distinguished from the naturally occurring resin acids in that they gelatinise when dissolved in alcohol and dilute aqueous ammonia and the resulting solution diluted with water. F. B.

Resins Employed in Embalming in Egypt and Carthage during the First Millenium B.C. Alexander Tschirch and Louis Reutter (*Arch. Pharm.*, 1912, 250, 170—185).—Copious references to the literature of the processes of embalming and the materials used by the ancients are given. Previous investigators have examined the materials employed by their appearance, odour, volatility, solubility, etc., but their deductions are untrustworthy, because, owing to the fact that the ancients frequently employed mixtures of resinous materials, the only certain method of examination is to isolate and analyse individual chemical substances.

Using this process, the authors have examined the resins obtained from embalmed Egyptian mummies, and have recognised storax (probably *Storax officinalis* or *Liquidambar orientalis*) by the isolation of cinnamic and benzoic acids, vanillin, and gum mastic by the isolation of *β*-masticic acid, *β*-masticonic acid, and resen, and Aleppo resin by the isolation of alepopinic acid, and asphalt, although the presence of the last cannot be proved definitely. Natron and sugar have also been identified, the latter probably being derived from the wine in which the corpses have been washed.

The same substances have been found in the materials used for embalming in Carthage. In addition, sandarac has also been (somewhat doubtfully) identified. One substance found in the embalming materials of Carthaginian, but never of Egyptian, mummies is incense. Amber has been found in the embalming material of a Phœnician mummy. The authors note with interest that the m. p.'s of the cinnamic acid, benzoic acid, and vanillin, and the rotatory and reducing powers of the sugar are the same as at the present time, although some of these substances are 3000 years old. C. S.

[The Glucoside of Aralia japonica.] LUCIEN DANZEL (*J. Pharm. Chim.*, 1912, [vii], 5, 530—534. Compare Houdas, Abstr., 1899, i, 772).—The leaves of *Aralia japonica* on extraction with alcohol and precipitation with water yield a glucoside *aralin*, which, after extraction with ether and several crystallisations from alcohol, is obtained in colourless, transparent crystals, m. p. 260°, $[\alpha]_D^{20} +52\cdot5°$. It is insoluble in water, contains no nitrogen, and is unacted on by nitric or hydrochloric acids. It does not reduce Fehling's solution. It is hydrolysed by dilute sulphuric acid, yielding dextrose and *aralidin*, a white, crystalline solid, m. p. 246—248°, insoluble in water and having an acid reaction to bases. It has no action on Fehling's solution. W. G.

Distribution of Amygdalin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1912, 250, 298—301).—In order to ascertain whether amygdalins from different sources are stereoisomeric, the author has determined the m. p., specific rotation, molecular weight, percentage of nitrogen, and rotation of the mandelic acid obtained after hydrolysis, of the amygdalins obtained from the kernels of the apricot, peach, plum, cherry, and from the apple and the quince. The results show that all these amygdalins are identical with that from the bitter almond. C. S.

The Glucosidic Acids of Convolvulin and the Composition of Crude *iso*Rhodeose. EMIL VOTOČEK (*Zeitsch. Zückerind. Böhm*, 1912, 36, 577—584).—Rhamnose has been identified among the products of acid hydrolysis of convolvulic acid. Convolvulin on alkaline hydrolysis yields α-methylbutyric acid and two glucosidic acids, crystalline convolvulic acid and amorphous purgic acid. The former yields dextrose, rhodeose, and rhamnose and hydroxypentadecoic acid on hydrolysis; the latter gives rise to decoic acid, hydroxylauric acid, and syrupy *iso*rhodeose.

The hydrogen cyanide addition product of *iso*rhodeose when oxidised with nitric acid does not form mucic acid. E. F. A.

Saponin of the White Soapwort. II. LEOPOLD ROSENTHALER and KNUT T. STRÖM (*Arch. Pharm.*, 1912, 250, 290—297. Compare Abstr., 1906, i, 32).—When heated with dilute sulphuric acid, gypsophila-saponin yields, in addition to sugars, a substance which ordinarily is called sapogenin; the authors, however, prefer the name *prosapogenin*. It has m. p. 207° (decomp.), crystallises in needles or prisms, has $[\alpha]_D^{18} +11\cdot92°$, forms a *semicarbazone*, m. p. 241°, and is converted by 2% sulphuric acid under pressure into *sapogenin*, $C_{24}H_{34}O_5$, m. p. 267—268°, crystalline rosettes. Sapogenin has $[\alpha]_D^{18} +90\cdot86°$, is a monobasic acid, forms a *methyl* ester, m. p. 192°, *diacetyl* derivative, m. p. 164—165°, and *semicarbazone*, m. p. 259—260° (decomp.), and yields, by oxidation with alkaline potassium permanganate at 60—70°, *as*-dimethylsuccinic acid and a small quantity of a volatile (fatty?) acid. C. S.

Preparation of Chlorophyll. VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm*, 1912, **36**, 574—576).—Ether does not extract chlorophyll from undamaged leaves, but from finely divided leaves the chlorophyll is extracted completely without difficulty.

Fresh leaves full of sap may be deprived of 70% of this by exposure for a short time in a tall, closed vessel to ether vapour. When pressed, without cutting up the leaves, the sap is removed as a brown fluid, the chlorophyll remaining in the residue.

Very little lecithin is extracted by ether in this way, whereas extraction with alcohol and shaking of this extract with benzene causes a good deal of lecithin to accompany the chlorophyll.

E. F. A.

The Chlorophyll Group. XVI. Anhydro-β-phyllotaonin HENRYK MALARSKI and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1912 **42**, 219—234).—According to Kózniewski and Marchlewski, the product obtained by the action of hydrochloric acid on alkachlorophyll, which was discovered by Schunck and called phyllotaonin, is a mixture containing an anhydride of lactam character which cannot be extracted from its ethereal solution by 15% hydrochloric acid, and a corresponding hydrated derivative which can be extracted by 4% hydrochloric acid. On these differences of properties, a method of separation of the two substances is founded. The lactam can be converted into the hydrated derivative by treatment with sodium hydroxide, and this substance on heating in solution can be reconverted into the anhydride. This anhydride is designated anhydro-β-phyllotaonin, and the authors give an account of their experiments for obtaining this substance pure. The chief operations are as follows: The chlorophyll is treated with 2% alcoholic potassium hydroxide. From the filtered clear solution the alkaneo-chlorophyll is precipitated by barium or calcium chloride. The precipitate, after extraction with ether, is treated with concentrated hydrochloric acid, in which it almost entirely dissolves. The filtered solution in acid is then diluted with water and neutralised with sodium carbonate, and the precipitate after drying is dissolved in chloroform. The chloroform solution is diluted with a large amount of ether; the solution thus obtained is extracted with 15% hydrochloric acid, and then with concentrated acid. The latter solution is then diluted with water and immediately extracted with ether. The residue from the last extract is then recrystallised from alcohol. The spectrum of the anhydrophyllotaonin is described in some detail, and a preliminary account is given of some of its chemical reactions. S. B. S.

Tannin. JOSEF HERZIG (*Ber.*, 1912, **45**, 1986).—The fact that dextrose was not obtained by Herzig and Renner (Abstr., 1909, i, 713) on hydrolysis of methylotannin with potassium hydroxide is not regarded as contrary to the possibility that tannin is a glucoside (compare Manning and Nierenstein, this vol., i, 566). E. F. A.

Transformations of Thiophen-2-aldehyde. E. GRISHKEWITSCH-TROCHIMOWSKY and IPPOLYT MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 570—581. Compare Abstr., 1911, i, 481).—Thiophen-

2-aldehyde readily forms a *sodium hydrogen sulphite* compound, $C_4H_3S\cdot CH(OH)\cdot O\cdot SO_3Na$.

The *semicarbazone*, $C_4H_3S\cdot CH\colon N\cdot NH\cdot CO\cdot NH_2$, forms white, silvery scales, m. p. 213° (decomp.).

The *azine*, $C_4H_3S\cdot CH\colon N\cdot N\colon CH\cdot C_4H_3S$, crystallises in yellow needles, m. p. 151—152°.

With acetophenone in presence of sodium methoxide, thiophen-2-aldehyde condenses, giving *thienylideneacetophenone*,

$$C_4H_3S\cdot CH\colon CH\cdot COPh,$$

which forms yellowish-green crystals, m. p. 59°. With bromine this compound yields the *dibromide*, $C_4H_3S\cdot CHBr\cdot CHBr\cdot COPh$, in colourless needles, m. p. 113° (decomp.).

Thienylideneacetone, $C_4H_3S\cdot CH\colon CH\cdot COMe$, m. p. 30—35°, forms a *dibromide*, $C_8H_8OBr_2S$, m. p. about 60° (decomp.).

Dithienylideneacetone, $C_4H_3S\cdot CH\colon CH\cdot CO\cdot CH\colon CH\cdot C_4H_3S$, obtained by the condensation of thienylideneacetone with thiophen-2-aldehyde in presence of sodium hydroxide, forms bright yellow plates, m. p. 119—120°, and yields a *tetrabromide*, $C_{13}H_{10}OBr_4S_2$, m. p. about 105° (decomp.).

Benzylidenethienylideneacetone, $C_4H_4S\cdot CH\colon CH\cdot CO\cdot CH\colon CHPh$, forms pale yellow needles, m. p. 100°, and gives a *tetrabromide*, $C_{15}H_{12}OBr_4S$, m. p. about 105° (decomp.).

Ethyl 4-*thienyl*-2 : 6-*dimethyldihydropyridine*-3 : 5-*dicarboxylate*,

$$NH{<}{\scriptstyle CMe\colon C(CO_2Et) \atop \scriptstyle CMe\colon C(CO_2Et)}{>}CH\cdot C_4H_3S,$$

obtained by the condensation of thiophen-2-aldehyde, ethyl acetoacetate, and ammonia in alcoholic solution, forms blue needles, m. p. 169—170°.

Oxidation of the preceding compound yields *ethyl* 4-*thienyl*-2 : 6-*dimethylpyridine* - 3 : 5 - *dicarboxylate*, $N{<}{\scriptstyle CMe\cdot C(CO_2Et) \atop \scriptstyle CMe\colon C(CO_2Et)}{>}C\cdot C_4H_3S$, which forms faintly yellow, shining needles, m. p. 76·5—77·5°, and gives a *hydriodide*, $C_{17}H_{19}O_4NS,HI$, m. p. about 160° (decomp.), and a *platinichloride*, $(C_{17}H_{19}O_4NS)_2,H_2PtCl_6$, decomposing at about 120°. From *silver* 4-*thienyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, the *hydrochloride* of 4-*thienyl*-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylic acid*, $N{<}{\scriptstyle CMe\cdot C(CO_2H) \atop \scriptstyle CMe\colon C(CO_2H)}{>}C\cdot C_4H_3S,HCl$, was prepared. The attempted preparation of 4-thienyl-2 : 6-dimethylpyridine by dry distillation of the potassium salt of the dicarboxylic acid with lime resulted in decomposition of the acid into hydrogen sulphide, carbon dioxide, and 2 : 6-dimethylpyridine.

The thiophen ring is found to be unstable towards potassium cyanide, attempts to prepare a compound analogous to benzoin by the condensation of thiophen-2-aldehyde with potassium cyanide being hence unsuccessful. T. H. P.

"Selenindigo" ("Bis-selenonaphthenindigo") and Aromatic Selenium Compounds. I. RUDOLF LESSER and R. WEISS (*Ber.*, 1912, **45**, 1835—1841).—A preliminary account of the results of successful endeavours to prepare compounds containing a selenium

atom in place of a sulphur atom. The products show, in general, similar chemical properties to the corresponding sulphur compounds, but differ from them in physiological effect.

A solution of potassium hydroselenide is treated with a diazotised solution of anthranilic acid, and the resultant diazo-compound decomposed by warming; on acidifying the hot solution there separates *diphenyldiselenide-di-*o*-carboxylic acid* ("*diselenodisalicylic acid*"), $Se_2(C_6H_4\cdot CO_2H)_2$, a pale yellow, crystalline substance, m. p. 296—297° (decomp.). The mother liquors contain *diphenylselenide-di-*o*-carboxylic acid*, $Se(C_6H_4\cdot CO_2H)_2$, pale yellow, microscopic needles, m. p. 228—229°. The diseleno-acid is reduced in alkaline solution by zinc dust to "*selenosalicylic acid* [*o-selenolbenzoic acid*], $SeH\cdot C_6H_4\cdot CO_2H$, which is stable only as the salt, and on acidification the diseleno-acid is re-obtained. If the reduced alkaline solution is introduced into a solution of the theoretical quantity of a salt of chloroacetic acid, the mixture warmed, and then precipitated by mineral acid, there is obtained a quantitative yield of o-*carboxyphenylselenolacetic acid*, $CO_2H\cdot C_6H_4\cdot Se\cdot CH_2\cdot CO_2H_7$, microscopic needles, m. p 233—234° (decomp.). Chlorosulphonic acid dissolves this substance to a red solution, which on treating with water precipitates a red *substance*, soluble in alkalis to a violet-blue solution.

When o-carboxyphenylselenolacetic acid is boiled with excess of acetic anhydride and some anhydrous potassium acetate, and the excess of acetic anhydride subsequently removed by distillation or by the addition of water, an *acetyl* compound is obtained, which by hydrolysis with sodium hydroxide solution yields 3-*hydroxyselenonaphthen*, $C_6H_4<\substack{C(OH)\\Se}>CH$, colourless, silky needles, m. p. 76—77°. This resembles the analogous hydroxythionaphthen in its main properties; by dissolving in alkali solution and oxidation with potassium ferricyanide, it is converted into "*selenindigo*" ("2 : 2-*bis-selenonaphthenindigo*") [2 : 2′-*bisoxyselenonaphthen*],

$$C_6H_4<\substack{CO\\Se}>C:C<\substack{CO\\Se}>C_6H_4;$$

compare Friedländer, Abstr., 1908, i, 371, 372, 673, 674); this is sparingly soluble in ordinary solvents, but separates from xylene in reddish-brown needles, which sublime undecomposed at 270° approx. and have m. p. 330—335°. It is reduced by alkali and hyposulphite to to a yellow vat which dyes cotton and wool violet-red.

Hydroxyselenonaphthen condenses likewise with isatin, and red silky needles of "2-*selenonaphthen*-3-*indole-indigo*" [3′-*indoxyl*-2-*selenonaphthen*-3-*one*], $C_6H_4<\substack{CO\\Se}>C:C<\substack{CO\\C_6H_4}>NH$ (which sublime undecomposed at approx. 250°, and have m. p. about 350°), separate immediately on warming an alcoholic solution of the two substances with a drop of piperidine. It gives a yellow vat with alkali and hyposulphite, which dyes a bluer shade than thioindgo scarlet.

"*Acenaphtheneselenonaphthenindigo*" [8-*oxy*-7-*oxyselenonaphthenyl-acenaphthene*], $C_6H_4<\substack{CO\\Se}>C:C<\substack{C_{10}H_6\\CO}$, prepared analogously to the

above, forms yellowish-red needles, which sublime at 220° approx., and have m. p. 272°; it gives, on reduction, a yellow vat.

If an intimate mixture of diphenyl-diselenide-di-*o*-carboxylic acid with phosphorus pentachloride is heated to melting and the benzene extract of the product saturated with ammonia, there is obtained a precipitate of *diphenyl-diselenide-di-*o*-carboxylamide*,

$$Se_2(C_6H_4\cdot CO\cdot NH_2)_2,$$

yellow needles, m. p. 265—266°. On boiling with a solution of potassium permanganate, this is oxidised to "*selenosaccharin*" (*benzoic selenonimide*), $C_6H_4<\begin{matrix}-CO-\\ SeO_2\end{matrix}>NH$, colourless needles, m. p. 227—228° (decomp.), which are sparingly soluble in water; the sweet taste of the sulphur analogue is entirely lacking. The imino-hydrogen is replaceable by metals, the salts with the alkalis being very soluble.

Oxidation of diphenyl-diselenide-di-*o*-carboxylic acid gives the parent substance of "selenosaccharin," *o-selenolbenzoic acid*, which is very easily soluble in water. D. F. T.

Compounds of Chloral Hydrate with Urotropine and Caffeine. ALBERT LEULIER (*J. Pharm. Chim.*, 1912, [vii], 6, 18—21).—Chloral hydrate in saturated aqueous solution combines with urotropine and caffeine, forming in each case two compounds according to the proportions of the reagents employed.

Monochloralurotropine, $C_6H_{12}N_4,C_2HOCl_3,H_2O$, crystallising in rhombohedra, and *dichloralurotropine*, $C_6H_{12}N_4,(C_2HOCl_3,H_2O)_2$, crystallising in needles, resemble one another in their properties. They are colourless and odourless, and very soluble in alcohol and water. They volatilise at about 100° without melting. They are both neutral substances, which reduce copper solutions and ammoniacal silver nitrate. With mineral acids they yield formaldehyde, and with alkalis the chloral is attacked, giving chloroform in the cold and carbylamine on heating.

Dichloralcaffeine, $C_8H_{10}O_2N_4,H_2O,(C_2HOCl_3,H_2O)_2$, m. p. 72—73°, on remaining loses 1 mol. of chloral and passes into *monochloralcaffeine*, $C_8H_{10}O_2N_4,H_2O,C_2HOCl_3,H_2O$, m. p. 92—93°. The latter compound dissolves in water, and in solution slowly dissociates on remaining, the caffeine separating out. In hot alcoholic solution it is completely dissociated. When heated at 100° all the chloral is driven off, leaving pure caffeine. W. G.

Ephedrine and ψ-Ephedrine. ERNST SCHMIDT and FRANZ W. CALLIESS (*Arch. Pharm.*, 1912, 250, 154—170).—The following results have been obtained during the course of unsuccessful experiments for the syntheses of ephedrine and ψ-ephedrine.

As the result of attempts to racemise the active bases, it has been found that ephedrine is almost unattacked by aqueous barium hydroxide at 210°, whilst ψ-ephedrine is converted by intramolecular change into ephedrine; the results are the same when alcoholic potassium hydroxide at 100—110° is employed. On the contrary, ephedrine is converted by concentrated sulphuric acid on the water-bath into ψ-ephedrine, whilst at the ordinary temperature ephedrine

and ψ-ephedrine are both converted by the acid in seventy-two hours into a substance (or substances) of the same rotatory power. By heating with acetic anhydride, ephedrine and ψ-ephedrine yield identical *acetyl* derivatives, m. p. 101° (*hydrochloride*, m. p. 176°, $[\alpha]_D^{20}$ 96·8°; *platinichloride*, m. p. 184°; *aurichloride*, m. p. 165°), which are shown to be *acetyl-ψ-ephedrine*,

OH·CHPh·CHMe·NMeAc.

During the acetylation, therefore, the ephedrine has changed to ψ-ephedrine.

The same change is effected by nitrous acid. The hydrochloride of either base reacts with sodium nitrite to form the same *nitroso*-compound, m. p. 80°, colourless needles, from which ψ-ephedrine hydrochloride is obtained by hydrolysis with 25% hydrochloric acid.

C. S.

Harmaline Derivatives. OTTO FISCHER and WALTER BOESLER (*Ber.*, 1912, 45, 1930—1934).—By the successive addition of pyridine and sodium acetate to a dilute acetic acid solution of harmaline and *p*-toluenediazonium chloride, *bis-p-tolueneazoharmaline*, $C_{27}H_{26}ON_6$, m. p. 182—183° (decomp.), reddish-brown needles, has been obtained. *Bisbenzeneazoharmaline*, decomp. about 180°, *bis-p-chlorobenzeneazoharmaline*, decomp. 185°, and *bis-p-bromobenzeneazoharmaline*, decomp. 200—203°, have been prepared in a similar manner. Harmine, *apo*harmine, and harminic acid do not form similar compounds.

Harmaline in 80—90% sulphuric acid is converted, after two days in darkness or six to seven hours in sunlight, into a *sulphonic acid*, $C_{13}H_{14}O_4N_2S$, yellow needles. When shaken with nitric acid, D 1·15, at the ordinary temperature, harmaline is converted into nitroharmaline (*acetyl* derivative, $C_{15}H_{15}O_4N_3$, m. p. 181° [decomp.], golden-yellow leaflets), *m*-nitroanisic acid, and nitro*apo*harminecarboxylic acid (Abstr., 1905, i, 229). Nitroharmaline is converted into nitroharmine by boiling dilute nitric acid, or, better, by potassium permanganate and dilute sulphuric acid.

C. S.

Chemical Action of Light. XXIII. Autoxidations. II. GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 619—621; *Ber.*, 1912, 45, 1842—1845. Compare this vol., i, 174).—On prolonged exposure to light, pyrrole undergoes complete decomposition into products which are largely tarry and from which the following compounds have been isolated: (1) a crystalline compound, $C_{12}H_{14}O_5N_2$, apparently derived from tripyrrole; (2) ammonium salts of undetermined composition, and (3) succinimide which has previously not been obtained from pyrrole and may be regarded as the ketonic form of the quinol of pyrrole,

$$NH\begin{cases}C(OH){:}CH\\ \quad\quad\quad\ \ |\\ C(OH){:}CH\end{cases}.$$

In the dark, pyrrole undergoes slight resinification.

Ethyl dihydrocollidinedicarboxylate (Hantzsch's ester) also undergoes autoxidation in presence of oxygen and water, yielding ethyl collidinedicarboxylate.

T. H. P.

Hæmopyrrole. LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1912, 79, 351—352).—Polemical. Reply to Fischer and Bartholomäus (this vol., i, 580). W. D. H.

The Solution of the Hæmopyrrole Question. HANS FISCHER and ERICH BARTHOLOMÄUS (*Ber.*, 1912, 45, 1979—1986. Compare this vol., i, 297, 384, 493, 580).—The constitution of a 2 : 3-dimethyl-4-ethylpyrrole has been rendered probable for hæmopyrrole: this is now confirmed by the synthesis of 2 : 3-dimethyl-4 : 5-diethylpyrrole.

By condensation of dipropionylmethane with oximinomethyl ethyl ketone, a pyrrole of the constitution $NH<\begin{matrix}CMe:CMe\\ CEt:C\cdot COEt\end{matrix}$ is obtained, from which, by the action of concentrated sulphuric acid, the propionyl group is eliminated and 2 : 3-dimethyl-5-ethylpyrrole obtained. This is entirely different from hæmopyrrole. On introduction of a second ethyl group, a diethyl pyrrole identical with that obtained from hæmopyrrole is obtained.

In addition a new pyrrole has been obtained from the hæmopyrrole mixture, namely, *cryptopyrrole* or 2 : 4-*dimethyl*-3-*ethylpyrrole*,

$$NH<\begin{matrix}CMe:CEt\\ CH=CMe\end{matrix}.$$

Cryptopyrrole picrate has m. p. 137—138°.

Dipropionylmethane is a colourless oil, b. p. 172—173°/711 mm., D^{20} 0·9445; it gives a reddish-brown coloration with ferric chloride in alcoholic solution.

4-*Propionyl*-2 : 3-*dimethyl*-5-*ethylpyrrole* crystallises in colourless needles, m. p. 118—119°; the absorption spectrum shows a broad band in the green.

2 : 3-*Dimethyl*-5-*ethylpyrrole* is a yellow oil, characterised by yielding an azo-dye with diazobenzenesulphonic acid, which forms bronze-coloured crystals. It forms a dimethyldiethylpyrrole, m. p. 106—107°. E. F. A.

The Synthesis of Tetramethylpyrrole. GIUSEPPE PLANCHER and T. ZAMBONINI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 598—600).—Two grams of acetyltrimethylpyrrole are heated to 220° in a sealed tube with a solution of 2 grams of sodium in 20 c.c. of absolute methyl alcohol. The product is precipitated with water, filtered in an atmosphere of nitrogen, dried in a vacuum, and crystallised from light petroleum; it then forms colourless crystals, m. p. 111°. This tetramethylpyrrole, $C_8H_{13}N$, has a fæcal odour, and rapidly darkens in air. The *picrate* has m. p. 128° (decomp.). C. H. D.

Syntheses of Phyllopyrrole. U. COLACICCHI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 489—493).—The acetyltrimethylpyrrole obtained by the action of heat on the dipyrrylmethane formed by the condensation of paracetaldehyde with 3-acetyl-2 : 4-dimethylpyrrole (compare this vol., i, 491) is not identical with 3-acetyl-2 : 4 : 5-trimethylpyrrole prepared by Knorr and Lange's method (Abstr., 1902, i, 821). When attempts were made to hydrolyse the latter compound with

alcoholic potassium hydroxide in a sealed tube, the products were found to contain phyllopyrolle (Willstätter and Asahina, this vol., i, 41), the acetyl group of the original derivative being replaced by ethyl. A similar replacement is effected by the action of sodium ethoxide on hydrazones (compare Knorr and Hess, Abstr., 1911, i, 1019) and on ketazines (compare Fischer and Bartholomäus, this vol., i, 50). The author has, indeed, obtained phyllopyrrole also from the ketazine corresponding with 3-acetyl-2 : 4 : 5-trimethylpyrrole.

3-*Acetyl*-2 : 4 : 5-*trimethylpyrrole*, $NH<\begin{matrix}CMe{:}CAc \\ CMe{:}CMe\end{matrix}$, obtained by reducing a mixture of molecular proportions of oximinomethyl ethyl ketone and acetylacetone with zinc dust in acetic acid solution, forms shining, colourless needles or prisms, m. p. 209—210°, and gives the characteristic pine splinter reaction.

The corresponding *ketazine*,

$$\begin{matrix}CMe{:}CMe \\ NH{-}CMe\end{matrix}>C{\cdot}CMe{:}N{\cdot}N{:}CMe{\cdot}C<\begin{matrix}CMe{:}CMe \\ CMe{\cdot}NH\end{matrix},$$

obtained by the action of hydrazine hydrate, forms prismatic crystals, m. p. about 305°.

Reduction by Knorr's method of a mixture of molecular proportions of oximinoacetylacetone and methyl ethyl ketone yields the diacetyldimethylpyrazine obtained by Wolff (Abstr., 1903, i, 203).

Phyllopyrrole is found to have m. p. 64—65°, and its picrate, 101—103°. T. H. P.

Action of Sodium Alkoxides on Esters of Pyrrolecarboxylic Acids. U. COLACICCHI and C. BERTONI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 653—656).—The authors find that, like acetyl, hydrazine, and ketazine residues in the pyrrole nucleus (preceding abstract), the carbethoxy-group can also be replaced by an alkyl group by the action of sodium alkoxide.

In this way they have succeeded in converting ethyl 2 : 3 : 5-trimethylpyrrole-4-carboxylate into either 2 : 3 : 5-trimethyl-4-ethylpyrrole (phyllopyrrole; compare Willstätter and Asahina, this vol., i, 41) or 2 : 3 : 4 : 5-tetramethylpyrrole, and in converting ethyl 2 : 4-dimethyl-3 : 5-dicarboxylate into 2 : 3 : 4 : 5-tetramethylpyrrole. T. H. P.

New Pyrogenic Transposition in the Pyrrole Group: Relative Stability to Heat of Isomeric Derivatives. U. COLACICCHI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 657—658).—When 3-acetyl-2 : 4-dimethylpyrrole is heated in a sealed tube at about 300°, it is transformed quantitatively into 5-acetyl-2 : 4-dimethylpyrrole. This is the first transference which has been observed of a group from one carbon atom to another of the pyrrole nucleus, and indicates that acyl derivatives of pyrrole with the acyl group in the 2 position are more stable than those with this group in the 1 or 3 position.

T. H. P.

Synthesis of 2 : 4-Dimethylpyrrole-5-acetic Acid and 2 : 4-Dimethylpyrrole-5-propionic Acid. HANS FISCHER and ERICH BARTHOLOMÄUS (*Ber.*, 1912, 45, 1919—1926).—The action of zinc dust

on a glacial acetic acid solution of β-oximinolævulic acid and ethyl acetoacetate, initially at 0° and finally on the water-bath, leads to the formation of 3-*carbethoxy*-2 : 4-*dimethylpyrrole*-5-*acetic acid*,

$$CO_2H\cdot CH_2\cdot C\negthickspace<\begin{matrix} CMe\cdot C\cdot CO_2Et \\ NH-CMe \end{matrix},$$

m. p. 152—153° (decomp.), slender needles. The substance yields ethyl 2 : 4 : 5-trimethylpyrrole-3-carboxylate by keeping in the fused state for some time, but is converted by hot moderately concentrated sulphuric acid into 2 : 4-*dimethylpyrrole*-5-*acetic acid*. This acid forms yellow, unstable crystals, and reacts with diazotised sulphanilic acid to form a well-crystallised, brown *azo*-compound, $C_{14}H_{15}O_5N_3S$, which exhibits the stability and the reactions characteristic of a member of the β-series.

β-Oximino-γ-acetylbutyric acid, ethyl acetoacetate, and zinc dust react in a similar manner to form 3-*carbethoxy*-2 : 4-*dimethylpyrrole*-5-*propionic acid*, $C_{12}H_{17}O_4N$, m. p. 119—120° (decomp.), white needles. The substance is converted by heating with moderately concentrated sulphuric acid into 2 : 4-*dimethylpyrrole*-5-*propionic acid*, which has not been obtained crystalline, but couples with diazobenzenesulphonic acid to form a crystalline *azo*-compound, $C_{15}H_{17}O_5N_3S$. This azo-dye is quite different from that obtained from phonopyrrolecarboxylic acid, which undoubtedly belongs to the α-series. Since the phonopyrrole obtained by the distillation of phonopyrrolecarboxylic acid yields an azo-dye belonging to the β-series, a migration of a group from the β- to the α-position must have occurred during the distillation (compare Piloty, Abstr., 1911, i, 92; Fischer and Bartholomäus, this vol., i, 384).

C. S.

Nature of Picolide and Pyrrocoline. MAX SCHOLTZ (*Ber.*, 1912, 45, 1718—1725. Compare this vol., i, 385).—Picolide condenses with benzaldehyde in acetic acid solution in presence of hydrogen chloride; the hydrochloride,

$$COMe\cdot N\colon C_8H_3\cdot CH(CHPhCl)\cdot COMe,$$

is formed first, and yields monobenzylidene picolide when boiled with alcohol.

By the action of nitric acid on picolide, one or two acetyl groups are replaced by nitro-groups according to the concentration of the acid. Both are yellow, crystalline compounds; the dinitro-derivative is perhaps a dinitropyrrocoline. A second acetyl group could not be eliminated from the mononitro-compound so as to form mononitropyrrocoline.

When heated with methyl iodide and methyl alcohol at 120°, pyrrocoline forms the methiodide of dimethylpyrrocoline,

$$C_8H_5Me_2N,MeI,$$

thus behaving similarly to 1-methylpyrrole.

When pyrrocoline reacts with isatin, in addition to the coloured compound previously described (*loc. cit.*), a colourless compound, derived from the interaction of two molecules of each component, is obtained.

Pyrrocoline condenses with simple ketones on warming in acetic

acid solution, yielding compounds composed of 2 mols. of pyrrocoline and 1 mol. ketone.

The pyrrole hydrogen in pyrrocoline can be replaced by acid radicles. Thus when boiled with acetic anhydride and sodium acetate, pyrrocolyl methyl ketone is formed, in which the position of the acetyl group is uncertain. It condenses with benzaldehyde to benzylideneacetylpyrrocoline.

Benzylidenepicolide, $NAc{:}C_8H_3({:}CHPh){\cdot}CO{\cdot}CH_3$, forms greenish-yellow crystals, m. p. 157°, dissolving in concentrated sulphuric acid with a deep red coloration; the *hydrochloride* is a red, crystalline mass, decomp. 125°.

Mononitropicolide, $C_{10}H_8ON{\cdot}NO_2$, separates in yellow needles, m. p. 196°.

Dinitropyrrocoline (?), $C_8H_5N(NO_2)_2$, crystallises in large, yellow plates, m. p. 229°.

The *methiodide* of *dimethylpyrrocoline* crystallises in colourless platelets, m. p. 180°.

The colourless *compound*, $C_{32}H_{22}O_3N_4$, of pyrrocoline and isatin forms colourless platelets, which are not melted at 300°.

The *compound*, $CMe_2(C_8H_6N)_2$, from pyrrocoline and acetone, is a yellow, crystalline powder, m. p. 244—246° to a black liquid.

The corresponding *compound*, $CMePh(C_8H_6N)_2$, from acetophenone, is a yellow microcrystalline powder, m. p. 98°.

Acetylpyrrocoline, $C_8H_6N{\cdot}COMe$, is a somewhat viscid, yellow oil, b. p. 195°/18 mm., 288°/760 mm.

Benzylideneacetylpyrrocoline crystallises in yellow needles, m. p. 127°, and dissolves in concentrated sulphuric acid with a blood-red coloration. E. F. A.

Syntheses in the Indole Group. III. Methylindole C- and N-Carboxylic Acids. BERNARDO ODDO (*Gazzetta*, 1912, 42, i, 361—375).—3-Methylindole reacts with magnesium ethyl bromide without heating, and the product is converted by carbon dioxide into 3-*methylindole*-1-*carboxylic acid*, $C_6H_4{<}{}^{\overline{\quad\;CMe\quad}}_{N(CO_2H)}{>}CH$, which forms a crystalline precipitate, m. p. 129° (decomp.). The *ethyl* ester,

$$C_{12}H_{13}O_2N,$$

prepared from the magnesium compound and ethyl chlorocarbonate, has b. p. 288·5° under atmospheric pressure, and 215°/11 mm. Prolonged heating converts it into the ester of the following acid.

3-*Methylindole*-2-*carboxylic acid*, $C_6H_4{<}^{CMe}_{NH-}{>}C{\cdot}CO_2H$, is prepared by heating the magnesium compound, obtained as above, in a stream of carbon dioxide, finally raising the temperature to 315—320°. The product is recrystallised from benzene containing a little ether, and then forms white needles, m. p. 164—165°. The *barium* salt,

$$(C_{10}H_8O_2N)_2Ba,$$

has been analysed.

2-*Methylindole*-3-*carboxylic acid*, obtained from 2-methylindole, the reaction with carbon dioxide being carried out in boiling toluene solution, crystallises from chloroform and has m. p. 174° (decomp.).

The *barium* salt has been analysed. The *ethyl* ester forms small needles, m. p. 135°. C. H. D.

Complex Salts of Quinoline with Uranyl Salts. GIUSEPPE INGHILLERI and G. GORI (*Atti R. Accad. Fisocritici, Siena*, 1909).—These salts are of the type $UO_2(C_9H_7N)_2X_2$, and are usually microcrystalline and yellow, those with an inorganic acid radicle being dark yellow or orange. The following have been prepared :

(1) The *nitrate*; in addition to the complex salt of normal type, one having the formula $C_9H_7N\cdot UO_2\cdot NO_3,5H_2O$, was obtained. (2) The *sulphate*. (3) The *acetate*; here, too, the *complex* salt,

$$C_9H_7N\cdot UO_2(C_2H_4O_2)_2,$$

exists besides the normal one. Uranyl and potassium acetates form the double salt, $(C_2H_3O_2)_2UO_2 + C_2H_3O_2K + 5H_2O$; the complexes, $(C_9H_7N)_2UO_2(C_2H_3O_2)_2 + 2C_2H_3O_2K$,

$$UO_2(C_2H_3O_2)_2 + C_2H_3O_2Na + 2H_2O,$$

and $(C_9H_7N)_2UO_2(C_2H_3O_2)_2 + 2C_2H_3O_2Na$ have also been prepared. (4) The *oxalates*, $(C_9H_7N)_2UO_2{:}C_2O_4$, $C_2O_4UO_2 + Na_2C_2O_4 + 3H_2O$, $(C_9H_7N)_2UO_2{:}C_2O_4 + 2Na_2C_2O_4$, and $(C_9H_7N)_2UO_2{:}C_2O_4 + 2K_2C_2O_4$. (5) The *tartrate*, $(C_9H_7N)_2UO_2{:}C_4H_4O_6$.

Calcium chloride forms with quinoline a crystalline compound, $CaCl_2,xC_9H_7N$, similar to that formed with ammonia, $CaCl_2,8NH_3$. T. H. P.

Synthesis of Quininic Acid and of 6-Methoxy-4-methylquinoline. AMÉ PICTET and R. R. MISNER (*Ber.*, 1912, **45**, 1800—1804).—4-Methylquinoline was obtained by Beyer (Abstr., 1886, 630) by the condensation of aniline with acetone and formaldehyde by means of concentrated hydrochloric acid. Attempts to improve the yield by the addition of oxidising agents, etc., have been unsuccessful.

By condensation in a similar manner of *p*-anisidine with acetone and formaldehyde, 6-methoxy-4-methylquinoline is obtained.

Quininic acid, $OMe\cdot C_6H_3{<}\begin{matrix}C(CO_2H){:}CH \\ N{=}{=}{=}{=}{=}CH\end{matrix}$, is prepared by condensing *p*-anisidine with formaldehyde and ethyl pyruvate, and subsequent hydrolysis of the ester formed.

When aniline is condensed with monochloroacetone and formaldehyde, 3-chloro-4-methylquinoline is obtained, and not the ω-chloro-compound. E. F. A.

Cyanocyclaminanes. V. Synthesis of Cinchonic and Quininic Acids. ADOLF KAUFMANN, HEINRICH PEYER [and R. WIDMER] (*Ber.*, 1912, **45**, 1805—1810. Compare Kaufmann and Widmer, Abstr., 1911, i, 749, 750).—6-Methoxyquinoline methosulphate interacts with potassium cyanide to form a cyanoquinolan, which is converted by iodine into the methiodide of 4-cyano-6-methoxyquinoline. On distillation in a vacuum, quininonitrile is obtained, which can be hydrolysed either by acids or alkalis in presence of hydrogen peroxide to quininic acid. Cinchononitrile is hydrolysed by the same process by way of the

amide to cinchonic acid. The synthetic acids are in every way identical with those obtained from the alkaloids.

4-*Cyano*-6-*methoxy*-1-*methylquinolan* separates in well formed, yellow crystals, m. p. 80—81°, which soon become brown and black on exposure to air.

4-*Cyano*-6-*methoxyquinoline methiodide* forms slender, lustrous, orange needles or dark cherry-red, stunted prisms, m. p. 198° (decomp.).

Quininonitrile crystallises in yellow, woolly needles, m. p. 157°; it is readily hydrolysed by alcoholic potassium hydroxide and hydrogen peroxide to quininic acid, m. p. 280°. E. F. A.

2:8-Diaminoacridine. LUDWIG BENDA (*Ber.*, 1912, 45, 1787—1799). —Diaminoacridine is prepared in quantity by the following series of operations (compare Gram, *Diss*, Jena, 1892). *p*:*p*-Diaminodiphenylmethane is nitrated to *p*:*p*-diamino-*o*:*o*-dinitrodiphenylmethane, and this reduced to *p*:*p*:*o*:*o*-tetraminodiphenylmethane, which was not isolated, but the crude product containing tin was heated under pressure at 135—140°. A crystalline tin double salt of diaminoacridine was thus obtained.

2:8-Diaminoacridine behaves similarly to its homologue, the base of the acridine yellow dyes; the hydrochloride is, however, soluble in cold water. It can be diazotised, but on boiling, brown, amorphous, insoluble products are obtained. To prepare dihydroxyacridine the diaminoacridine is heated with 45% sulphuric acid in sealed tubes at 195°. The tetra-azoacridine prepared by means of nitrosylsulphuric acid can be degraded to acridine.

With formaldehyde and aromatic bases, diaminoacridine forms at first a sparingly soluble, orange condensation product of the acridine and formaldehyde alone; on warming, the amine enters into the reaction. The dyes have a deeper hue than the original diaminoacridine, and dye egg-yellow and orange to brown shades. The formula of these dyes is not yet established.

2:8-Diamino-10-methylacridinium chloride has a very intense trypanocidal action, being at least three times as effective as the homologue from acridine yellow. It has been tried on man in cases of sleeping sickness with good effect.

Diaminoacridine crystallises from water in very long, brownish-yellow needles or slender, matted needles, according to the rate of cooling. On heating, it begins to darken at 260°, m. p. 283° (decomp.). The sulphate forms red, matted needles.

2:8-*Dihydroxyacridine* crystallises in slender, orange needles with a bronze lustre, which becomes red at 275°, but have not melted at 300°. It dissolves in concentrated sulphuric acid with a bluish-green fluorescence.

2:8-*Diamino*-10-*methylacridinium chloride* forms long, red prisms dissolving in water to a yellow solution, which fluoresces green only when much diluted. It has a very bitter taste, about double that of 2:8-diaminoacridine. The *sulphate* crystallises in red needles.

On heating with 45% sulphuric acid a *dihydroxy*-compound, crystallising as hydrochloride in orange-red, matted needles, is obtained. An

anhydride, composed of two molecules of the 2 : 8-dihydroxyacridinium base less a molecule of water, forms lustrous, orange-red needles, which become red at 245° and sinter at 260—265°, m. p. 275°.

E. F. A.

Benz*iso*oxazoles. WALTHER BORSCHE (*Annalen*, 1912, **390**, 1—29).—The author has attempted to prepare from methyl 5-nitrobenz*iso*oxazole-2-carboxylate (Abstr., 1909, i, 385) the first representative of a benz*iso*oxazole unsubstituted in the heterocyclic nucleus, but unsuccessfully, since the hydrolysis of the ester, whether in acid, alkaline, or neutral solution, is always accompanied by fission of the heterocyclic ring.

[With PAUL OPPENHEIMER.]—The hydrolysis of the ester by aqueous alcoholic 20% sodium hydroxide, followed by acidification, yields 4-*nitro-2-hydroxyphenylglyoximic acid*,

$$NO_2{\cdot}C_6H_3(OH){\cdot}C(\colon NOH){\cdot}CO_2H,$$

m. p. 166—167° (decomp.). The same substance is obtained by hydrolysing the ester with dilute sulphuric acid.

5-*Nitrobenz*iso*oxazole-2-carboxylamide*, $C_8H_5O_4N_3$, m. p. 189—190°, obtained from the ester and alcoholic ammonia at 100°, is also converted into the nitrohydroxyphenylglyoximic acid by concentrated sulphuric acid and concentrated aqueous sodium nitrite.

4-*Nitrosalicylonitrile*, $NO_2{\cdot}C_6H_3(OH){\cdot}CN,H_2O$, m. p. 140—160° (decomp.), the preparation of which from methyl 5-nitrobenz*iso*oxazole-2-carboxylate, from 4-nitro-2-hydroxyphenylglyoximic acid, from 2 : 4-dinitrotoluene, or from 2 : 4-dinitrobenzaldoxime is described, has been converted into the *acetyl* derivative, m. p. 100°, by boiling acetic anhydride, into the *benzoyl* derivative, m. p. 122°, by benzoyl chloride in pyridine, into ? : ?-*dibromo-4-nitrosalicylonitrile*,

$$C_7H_2O_3N_2Br_2,$$

m. p. 193° (decomp.), by bromination in acetic acid and sodium acetate, and into 4 : ?-*dinitrosalicylonitrile*, m. p. 174°, by nitric acid, D 1·52, at 0°. 4-*Aminosalicylonitrile*, $NH_2{\cdot}C_6H_3(OH){\cdot}CN$, m. p. 182°, yellowish-white needles, is obtained by reducing the nitro-compound by tin, alcohol, and concentrated hydrochloric acid; its *dibenzoyl* derivative has m. p. 198—199°.

4-*Nitrosalicylic acid*, m. p. 235° (decomp.), is obtained in about 80% yield by heating methyl 5-nitrobenz*iso*oxazole-2-carboxylate with 5*N*-hydrochloric acid at 150°; it forms an *ethyl* ester, m. p. 87°, and an *amide*, m. p. 192—194°, and is converted by nitric acid, D 1·52, into trinitroresorcinol (styphnic acid).

When treated with sodium ethoxide, a well-cooled alcoholic solution of 2 : 4-dinitrobenzyl methyl ketone and *iso*amyl nitrite yields 5-*nitro-2-acetylbenz*iso*oxazole*, $NO_2{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{CAc}{O}{>}N$, m. p. 135—136°, together with 4-nitrosalicylonitrile as a by-product; the amount of the latter increases at higher temperatures.

2 : 4-*Dinitro-a-oximinobenzyl methyl ketone*,

$$C_6H_3(NO_2)_2{\cdot}C(\colon NOH){\cdot}COMe,$$

m. p. 156°, obtained by treating a benzene solution of 2 : 4-dinitrobenzyl methyl ketone at 0° with hydrogen chloride and *iso*amyl nitrite,

forms a *semicarbazone*, m. p. 226° (decomp.), and a *phenylhydrazone*, m. p. 197—198° (decomp.), red needles. It is converted by hot alcoholic sodium ethoxide into 5-nitro-2-acetylbenz*iso*oxazole (*phenylhydrazone*, m. p. 192—193°), which is stable to boiling alcohol and 5*N*-hydrochloric acid, but is hydrolysed rapidly by 5% sodium hydroxide, yielding 4-nitrosalicylonitrile and acetic acid.

2 : 4-*Dinitrophenylacetyl chloride*, $C_6H_3(NO_2)_2\cdot CH_2\cdot COCl$, m. p. 77°, obtained from the acid and thionyl chloride in boiling benzene, is converted by ethereal ammonia into 2 : 4-*dinitrophenylacetamide*, m. p. 180°, and reacts in benzene with aluminium chloride to form, ultimately, ω-2 : 4-*dinitrophenylacetophenone*, $C_6H_3(NO_2)_2\cdot CH_2\cdot COPh$, m. p. 135—136°. The latter is converted, in benzene, by hydrogen chloride and *iso*amyl nitrite into the *oximino*-compound,

$$C_6H_3(NO_2)_2\cdot C(:NOH)\cdot COPh,$$

m. p. 174° (decomp.), which reacts with boiling alcoholic sodium ethoxide to form 5-*nitro*-2-*benzoylbenz*iso*oxazole*, m. p. 157—158°, which partly decomposes during the reaction into ethyl benzoate and 4-nitrosalicylonitrile. C. S.

The Action of Aldehydes on Pyrrole Compounds. U. Colacicchi and C. Bertoni (*Atti R. Accad. Lincei*, 1912, [v], **21**, i, 600—604. Compare Colacicchi, Abstr., 1911, i, 1030).—Phenylpyrrole condenses with paraldehyde, yielding a yellow powder, $C_{12}H_{11}N$, decomposing at 195—200°, together with a small quantity of a second substance, insoluble in light pretroleum. The *compound* obtained from phenylpyrrole and formaldehyde, $C_{11}H_9N$, is amorphous, and decomposes at about 100°, whilst that from propaldehyde, $C_{13}H_{13}N$, decomposes at 145°.

Bis-3-*acetyl*-2 : 4-*dimethylpyrrylpropane*, $(OAc\cdot C_4NHMe_2)_2CHEt$, prepared from 3-acetyl-2 : 4-dimethylpyrrole and propaldehyde in presence of zinc chloride, crystallises from alcohol in small, white plates, m. p. 216—217°.

Bis-3-*acetyl*-2-*phenyl*-4-*methylpyrrylmethane*, $(OAc\cdot C_4NHPhMe)_2CH_2$, forms colourless prisms, m. p. 252—253°. *Bis*-5-*benzoyl*-2 : 4-*dimethylpyrrylpropane*, $(OBz\cdot C_4NHMe_2)_2CHEt$, crystallises from alcohol in glistening, yellow leaflets, m. p. 245—246°. C. H. D.

Syntheses in the Pyrrole Group. IV. Pyridine–pyrrole Bases. Bernardo Oddo (*Gazzetta*, 1912, **42**, i, 346—352. Compare Abstr., 1910, i, 426).—Magnesium pyrryl iodide reacts with nicotinic chloride, suspended in ether. After remaining overnight, the pasty mass is mixed with ice and made alkaline with sodium hydrogen carbonate. The ether is then removed, and the residue extracted with boiling water.

3-*Pyridyl* 2-*pyrryl ketone*, $C_5NH_4\cdot CO\cdot C_4NH_4$, crystallises from aqueous alcohol in white needles, m. p. 132°. The *aurichloride* is an orange precipitate, m. p. 165° ; the *platinichloride*,

$$(C_{10}H_8ON_2)_2,H_2PtCl_6,$$

is granular, and decomposes at 235° without melting. The *picrate* crystallises from boiling water, and has m. p. 228—230° (decomp.). The *silver* salt, $C_5NH_4\cdot CO\cdot C_4H_3NAg$, is a white precipitate.

A solution of the ketone in ether reacts with magnesium ethyl iodide, forming the *compound*, $MgEt\cdot C_5NH_4I\cdot CO\cdot C_4NH_3\cdot MgI,Et_2O$.

2-*Pyridyl 2-pyrryl ketone*, prepared in the same manner from picolinic chloride, forms bright yellow crystals, m. p. 74°. The *picrate* forms yellow, silky needles, m. p. 85°, and the *platinichloride* a yellow precipitate, not melted at 265°. The *aurichloride* and the *silver* derivative have been prepared. C. H. D.

Thiele's Theory and Indigotin. M. TSCHILIKIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 498—514).—The author shows by means of a number of examples that Thiele's theory of residual valency (Abstr., 1899, i, 554) readily explains the transformations which indigotin and its derivatives undergo. T. H. P.

Quinoline-indole Dyes. WALTER KÖNIG (*J. pr. Chem.*, 1912, **85**, [ii], 514—522).—2-Methylindole-3-aldehyde readily condenses with salts of the following bases, yielding yellow, red, bluish-red to blue basic dyes: 2-methylquinoline, 4-methylquinoline, 2-methylpyridine, 4-methylpyridine, 2 : 5-dimethylpyridine, and 5-methylacridine. The dyes form periodides, and on treatment with alkalis yield strongly coloured bases.

The present paper deals with the dyes derived from 2- and 4-methylquinoline methiodides and methoperchlorates.

The *dye*, $\begin{matrix}CH{=\!=}CH\\ | \\ C_6H_4\cdot NMeI\end{matrix}\!\!>C\cdot CH{:}CH\cdot C<\!\!\begin{matrix}C_6H_4\\ CMe\end{matrix}\!\!>NH$, obtained by condensing the aldehyde with 2-methylquinoline methiodide by means of piperidine in methyl alcoholic solution, forms small, brownish-red crystals, m. p. 280°, and is converted by aqueous sodium hydroxide into the corresponding *dye base*, which forms bluish-green needles of a golden lustre.

2-*Methylquinoline methoperchlorate*, $C_{11}H_{12}O_4NCl$, prepared from 2-methylquinoline methiodide and sodium perchlorate in aqueous solution, crystallises in almost colourless prisms, m. p. 154°, and condenses with 2-methylindole-3-aldehyde, yielding the *dye*,

$$C_{21}H_{19}O_4N_2Cl,$$

which forms microscopic, brownish-red needles, m. p. above 300° (decomp.). The *chloride*, $C_{21}H_{19}N_2Cl$, obtained by shaking a suspension of the preceding perchlorate in acetone with 20% aqueous sodium hydroxide, and subsequently treating the acetone solution of the dye base with hydrochloric acid and sodium chloride, is orange-red in colour, has m. p. above 290°, and forms a *mercurichloride*.

The condensation of 4-methylquinoline methiodide and 2-methylindole-3-aldehyde by means of piperidine in methyl-alcoholic solution yields the bluish-red *dye*, $\begin{matrix}NMeI\cdot C_6H_4\\ \| \\ CH{-\!-}CH\end{matrix}\!\!>C\cdot CH{:}CH\cdot C<\!\!\begin{matrix}C_6H_4\\ CMe\end{matrix}\!\!>NH$, which has m. p. above 300°, and crystallises with methyl alcohol (1 mol.).

The corresponding *perchlorate* yields with sodium hydroxide the *dye base*, $\begin{matrix}NMe\cdot C_6H_4\\ | \\ CH{=\!=}CH\end{matrix}\!\!>C{:}CH\cdot CH{:}C<\!\!\begin{matrix}C_6H_4\\ CMe\end{matrix}\!\!>N$. This crystallises in

lustrous, blue needles, m. p. 240° (decomp.), which lose their metallic lustre and become brown on exposure to air. From chloroform it separates in lustrous, green needles, containing 2 mols. of the solvent, which is removed at 160°. The colour of its solutions varies greatly with the nature of the solvent, being yellowish-red in water, reddish-violet in alcohol, bluish-violet in chloroform, and blue in pyridine and nitrobenzene. In aqueous solution, it undergoes partial transformation into a yellow *substance*, which crystallises in needles of a golden lustre, and is converted by acids into the original dye. F. B.

A New Method of Preparing Cyclamine-aldehydes and -alcohols. ADOLF KAUFMANN and LOUIS G. VALLETTE (*Ber.*, 1912, 40, 1736—1742).—Whereas 5-methylacridine readily reacts with nitrosodimethylaniline, the latter does not interact with quinaldine, lepidine, or α-picoline. The quaternary salts of these bases, however, readily take part in the condensation. Abnormally here the reactivity of the methyl group is greatly increased by the saturation of the nitrogen; thus quinaldine ethiodide condenses with nitrosodimethylaniline, particularly in the presence of a few drops of piperidine, with the formation of a reddish-violet colour. The *condensation product* forms green needles, decomp. 200°; it is decomposed by mineral acids into *as*-dimethyl-*p*-phenylenediamine and quinoline-2-aldehyde ethiodide.

Quinaldine ethiodide condenses with nitroso-naphthol, forming an intense olive-green solution, and also with nitrosoantipyrine.

The *methiodide* of α-picoline crystallises in long, colourless needles, m. p. 224°; it condenses with nitrosodimethylaniline to a red solution, from which the condensation product crystallises, +Et·OH, in green needles, m. p. 185° (decomp.). It becomes red on drying in the oven. Picoline ethiodide behaves similarly.

Lepidine methiodide condenses to a compound of coppery lustre, which dissolves in alcohol with an intense blue coloration.

The condensation product of nitrosodimethylaniline with 5-methylacridine forms coarse, orange-red crystals, m. p. 234°, and slender plates, m. p. 210—211°. When decomposed by acids, acridine-5-aldehyde (Bernthsen and Muhlert, Abstr., 1887, 850), m. p. 148°, is obtained. The *anil* crystallises in yellowish-brown platelets, m. p. 163°; the *oxime* forms yellow needles, m. p. 247° (decomp.), and yields a *hydrochloride* crystallising in yellowish-red needles, m. p. 252° (decomp.).

The *aldehyde* from the quinaldine ethiodide condensation product was characterised as *phenylhydrazone*; this formed red, stunted needles, m. p. 245°.

The methiodide of the dimethylaminoanil of pyridine-2-aldehyde was hydrolysed in a similar manner; the *phenylhydrazone* obtained crystallised in orange-yellow needles with a blue reflex, m. p. 244° (decomp.). E. F. A.

Diacetylfurazan. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 659—666).—The author finds that when diacetylglyoxime (compare Thal, Abstr., 1892, 1074) is fused, it loses water, yielding

diacetylfurazan, $\begin{matrix} CAc:N \\ | \\ CAc:N \end{matrix}\!\!>\!O$, which may also be obtained by dissolving glyoxime in acetic anhydride.

Schmidt and Widman (Abstr., 1909, i, 524) obtained from acetonylacetone a compound which they described as diacetylfurazan, but which gives only a monophenylhydrazone and a monosemicarbazone. The author shows that this compound is identical with the one obtained by Angeli (Abstr., 1891, 890) by the action of concentrated nitric acid on acetonylacetone; its constitution is not determined.

Diacetylfurazandiphenylhydrazone, $C_{18}H_{18}ON_6$, m. p. 210°, the *dioxime*, $C_6H_8O_3N_4$, m. p. 128°, and the *disemicarbazone*, $C_8H_{12}O_3N_8$, decomposing at 239—240°, were prepared. Oxidation of diacetylfurazan by means of permanganate yields the furazandicarboxylic acid described by Wolff (Abstr., 1895, i, 192). T. H. P.

Dicyclic Compounds and their Comparison with Naphthalene. KARL FRIES (*Annalen*, 1912, **389**, 305—398).—Zincke has observed that derivatives of dicyclic compounds containing one benzenoid and one heterocyclic nucleus (1 : 2 : 3-benztriazole, 2 : 1 : 3-benztriazole, benziminoazole, and indazole) exhibit an astonishing similarity to the corresponding derivatives of naphthalene (Abstr., 1910, i, 140). With the object of seeing how extensive in reality is the agreement between such dicyclic systems and naphthalene, or whether the typical distinctions in behaviour between derivatives of benzene and the corresponding derivatives of naphthalene may not also be existent in such systems, the author has described in this communication the behaviour of derivatives of *N*-phenyl-ψ-azoiminobenzene [2-phenyl-2 : 1 : 3-bentriazole], *N*-phenylazoiminobenzene [1-phenyl-1 : 2 : 3-benztriazole], 4 : 7-dimethyl-1 : 2 : 3-benztriazole, and 3 : 3-diphenylcoumaranone.

As criteria of difference of behaviour between a benzene derivative and the corresponding naphthalene compound, the author selects (i) the reduction of naphthalene, (ii) the action of chlorine, nitric acid, and diazonium salts on α-halogenated or alkylated β-naphthols, (iii) the oxidation of 2 : 3-dihydroxynaphthalene and its derivatives. With regard to (ii), it is known that chlorine converts β-naphthol and 1-methyl-β-naphthol respectively into 1 : 1-dichloro-2-ketodihydronaphthalene and 1-chloro-2-keto-1-methyldihydronaphthalene (Abstr., 1908, i, 730), that nitric acid converts 1-bromo-β-naphthol into 1 : 2-bromonaphthaquinonitrole and 1-methyl-β-naphthol into 1 : 2-methylnaphthaquinonitrole (Abstr., 1906, i, 190), and that β-naphthols with substituents in position 1 do not, as a rule, couple with diazonium salts. With regard to (iii), 2 : 3-dihydroxynaphthalene and its halogenated derivatives are, unlike the catechols, not directly oxidised to *o*-quinones (Zincke and Fries, Abstr., 1904, i, 1008). The author finds that the benztriazoles exhibit the widest similarity in behaviour to the corresponding naphthalene derivatives, that the resemblance in properties of indazoles and naphthalene compounds is more superficial than real, and that coumaranones behave entirely like benzene derivatives.

1-*Bromo*-1-*nitro*-2-*ketodihydronaphthalene*, $C_{10}H_6O_3NBr$, m. p. 74°, is obtained by addition of nitric acid, D 1·52, to a chloroform solution

of 1-bromo-β-naphthol at 0°. By heating its solution in an indifferent solvent, β-naphthaquinone is very conveniently obtained in good yield, but cannot be kept for many hours, owing to the presence of some impurity which causes it to become tarry. The bromonitro-ketone is converted into 1 : 6-dinitro-β-naphthol by keeping its solution in glacial acetic acid, and into 1-nitro-β-naphthol by treating its solution in acetone with aqueous sodium carbonate.

[With E. ROTH.]—4-*Chloro-5-acetylamino-2-phenyl-2 : 1 : 3-benztriazole*, $NPh{<}\begin{smallmatrix}N\\|\\N\end{smallmatrix}{>}C_6H_2Cl\cdot NHAc$, m. p. 219°, leaflets, is obtained by passing chlorine into a hot solution of 5-acetylamino-2-phenyl-2 : 1 : 3-benztriazole containing sodium acetate. By hydrolysis it yields 4-*chloro-5-amino-2-phenyl-2 : 1 : 3-benztriazole*, $C_{12}H_9N_4Cl$, m. p. 153°, the solutions of which exhibit a greenish-blue fluorescence which disappears on the addition of acids or alkalis. By the reduction of 6-chloro-5-nitro-2-phenyl-2 : 1 : 3-benztriazole by tin and hydrochloric acid, the authors obtain a *dichloroaminophenylbenztriazole*, $C_{12}H_8N_4Cl_2$, m. p. 178°, not the 6-chloro-5-amino-2-phenyl-2 : 1 : 3-benztriazole described by Zincke and Scharff (Abstr., 1910, i, 140). Zincke and Scharff's compound, m. p. 229°, not 221—222° as stated, is formed when the reducing agent is iron and acetic acid.

The diazotisation of 5-amino-2-phenyl-2 : 1 : 3-benztriazole in concentrated sulphuric acid by sodium nitrite in concentrated sulphuric acid yields 2-*phenyl-2 : 1 : 3-benztriazole-5-diazonium sulphate*,

$$C_{12}H_8N_5\cdot HSO_4,$$

m. p. 142° (decomp.), which can be crystallised from 2N-sulphuric acid, and couples normally with dimethylaniline or R-salt. By treating a solution of the diazonium sulphate in 6 parts (by vol.) of concentrated sulphuric acid with 1·5 parts of ice and then heating, 5-*hydroxy-2-phenyl-2 : 1 : 3-benztriazole*, $NPh{<}\begin{smallmatrix}N\\|\\N\end{smallmatrix}{>}C_6H_3\cdot OH$, m. p. 177°, is obtained in about 60% yield. The hydroxy-compound, which forms an *acetyl* derivative, m. p. 98°, is converted, by treating its solution in dilute sodium hydroxide with sodium nitrite and then with dilute sulphuric acid at 0°, into 4-*nitroso-5-hydroxy-2-phenyl-2 : 1 : 3-benztriazole*, decomp. 185°, which forms metallic derivatives resembling those of nitroso-β-naphthol in colour and behaviour.

By passing the calculated quantity of chlorine into its solution in glacial acetic acid, 5-hydroxy-2-phenyl-2 : 1 : 3-benztriazole yields 4-*chloro-5-hydroxy-2-phenyl-2 : 1 : 3-benztriazole*,

$$NPh{<}\begin{smallmatrix}N\\|\\N\end{smallmatrix}{>}C_6H_2Cl\cdot OH,$$

m. p. 149°, which is converted by further chlorination in the same solvent into 4 : 4-*dichloro-5-keto-2-phenyl-4 : 5-dihydro-2 : 1 : 3-benztriazole*, $NPh{<}\begin{array}{l}N\cdot C\cdot CCl_2\cdot CO\\ | \quad \| \qquad\quad |\\ N\cdot C\cdot CH{=}CH\end{array}$, m. p. 165°, yellow plates, which is reconverted into the chlorohydroxyphenylbenztriazole by reduction with stannous chloride. 4-*Bromo-5-hydroxy-2-phenyl-2 : 1 : 3-benztriazole*, $C_{12}H_8ON_3Br$, m. p. 129° (*acetyl* derivative, m. p. 160°), obtained in a similar manner to the chloro-compound, is converted in

cold chloroform solution by nitric acid, D 1·52, into 4-*bromo*-4-*nitro*-5-*keto*-2-*phenyl*-4 : 5-*dihydro*-2 : 1 : 3-*benztriazole*,

$$NPh<\begin{matrix}N\cdot C\cdot CBr(NO_2)\cdot CO \\ N\cdot C\cdot CH=\!=\!=\!=CH\end{matrix},$$

m. p. about 150°, which is converted in cold acetone into 4-*nitro*-5-*hydroxy*-2-*phenyl*-2 : 1 : 3-*benztriazole*, $C_{12}H_8O_3N_4$, m. p. 145°, yellow needles, by aqueous sodium carbonate, and in boiling benzene into 4 : 5-*diketo*-2-*phenyl*-4 : 5-*dihydro*-2 : 1 : 3-*benztriazole*, orange-yellow crystals, which sinters at about 160°, but is not melted at 340°. This orthoquinone develops a dark green coloration with alkalis, yields the *diazine*, $C_{18}H_{11}N_5$, m. p. 225°, yellow needles, with *o*-phenylenediamine, and is reduced by acetic acid and zinc to 4 : 5-*dihydroxy*-2-*phenyl*-2 : 1 : 3-*benztriazole*, m. p. 189°, colourless needles (*diacetyl* derivative, m. p. 158°).

When an alcoholic solution of 5-chloro-2 : 4-dinitroacetanilide is boiled with phenylhydrazine and hydrated sodium acetate, the initially formed hydrazine is ultimately converted into 5-*nitro*-6-*acetylamino*-2-*phenyl*-2 : 1 : 3-*benztriazole*, m. p. 225°, orange needles, by the hydrolysis of which is produced 5-*nitro*-6-*amino*-2-*phenyl*-2 : 1 : 3-*benztriazole*, $NPh<\begin{matrix}N\\ N\end{matrix}>C_6H_2(NO_2)\cdot NH_2$, m. p. 236°, glistening black prisms. Its reduction by hydrochloric acid and stannous chloride in excess yields 5 : 6-*diamino*-2-*phenyl*-2 : 1 : 3-*benztriazole*, m. p. 244°, colourless crystals, solutions of which exhibit a strong blue fluorescence which disappears on the addition of acids or alkalis. The *diacetyl* derivative, m. p. 286° (decomp.), is converted by boiling hydrochloric acid into the *iminazole*, $NPh<\begin{matrix}N\\ N\end{matrix}>C_6H_2<\begin{matrix}N\\ NH\end{matrix}>CMe$, m. p. 256°. An alcoholic solution of the diamime is converted by sodium nitrite and acetic acid into the *azoimide*, $NPh<\begin{matrix}N\\ N\end{matrix}>C_6H_2<\begin{matrix}N\\ NH\end{matrix}>N$, m. p. about 280°, sintering at 250°, and by benzil into the *compound*, $NPh<\begin{matrix}N\\ N\end{matrix}>C_6H_2<\begin{matrix}N\cdot CPh\\ N\cdot CPh\end{matrix}$, m. p. above 300°, yellow needles.

4 : 4 : 7 : 7-*Tetrachloro*-5 : 6-*diketo*-2-*chlorophenyl*-4 : 5 : 6 : 7-*tetrahydro*-2 : 1 : 3-*benztriazole*, $C_6H_4Cl\cdot N<\begin{matrix}N\\ N\end{matrix}>C_6Cl_4O_2,\frac{1}{2}H_2O$, m. p. 155° (decomp.), is obtained by exhaustively chlorinating an emulsion of the stannichloride of the preceding diamine in acetic and concentrated hydrochloric acids. It is reduced by stannous chloride and acetic and hydrochloric acids to 4 : 7-*dichloro*-5 : 6-*dihydroxy*-2-*chlorophenyl*-2 : 1 : 3-*benztriazole*, $C_6H_4Cl\cdot N<\begin{matrix}N\\ N\end{matrix}>C_6Cl_2(OH)_2$, m. p. 270°, long needles, which is converted into, not an orthoquinone, but colourless products by many oxidising reagents. 5-Chloro-2 : 4-dinitroaniline, when boiled with phenylhydrazine under the conditions in which its acetyl derivative yields a phenyl-2 : 1 : 3-benztriazole, is converted into 4 : 6-*dinitro*-3-*aminodiphenylhydrazine*, $NHPh\cdot NH\cdot C_6H_2(NO_2)_2\cdot NH_2$, m. p. 193°, orange needles or prisms (*acetyl* derivative, m. p. 194°

decomp.), which is oxidised by ferric chloride and boiling glacial acetic acid to 4 : 6-*dinitro*-3-*aminoazobenzene*,

$$NPh\!:\!N{\cdot}C_6H_2(NO_2)_2{\cdot}NH_2,$$

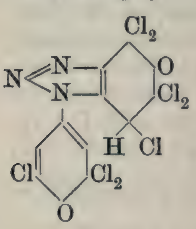
m. p. 200°, red needles (*acetyl* derivative, m. p. 175°).

3-*Chloro*-4 : 6-*dinitrophenol*, m. p. 92°, obtained by boiling 1 : 3-dichloro-4 : 6-dinitrobenzene with aqueous sodium carbonate, is unchanged by phenylhydrazine and sodium acetate in boiling alcohol, whilst its *acetyl* derivative, m. p. 69°, is simply hydrolysed under the same conditions.

[With J. Empson].—The nitration by sulphuric and nitric acids at 0° of 5-acetylamino-1-phenyl-1 : 2 : 3-benztriazole yields the *acetyl* derivative, m. p. above 300°, yellow needles, of 5-*amino*-1-p-*nitrophenyl*-1 : 2 : 3-*benztriazole*, $NO_2{\cdot}C_6H_4{\cdot}N\overset{N:N}{\diagup\!\!\!-\!\!\!-\!\!\!\diagdown}C_6H_3{\cdot}NH_2$, m. p. above 300°, orange-yellow needles, the reduction of which by stannous chloride and acetic acid yields 5-*amino*-1-p-*aminophenyl*-1 : 2 : 3-*benztriazole*, colourless needles, m. p. about 60°, re-solidifying at about 90°, and melting again at 154°.

The nitration of 5-acetylamino-1-phenyl-1 : 2 : 3-benztriazole by nitric acid, D 1·52, alone yields a dinitro-compound, decomp. 175°, yellow needles, which appears to be 4-*nitro*-5-*nitroamino*-1-*phenyl*-1 : 2 : 3-*benztriazole*, $C_{12}H_8O_4N_6$.

By warming a solution of 5-amino-1-phenyl-1 : 2 : 3-benztriazole with acetic anhydride, adding aqueous sodium acetate, and passing chlorine into the boiling solution, 4-*chloro*-5-*acetylamino*-1-*phenyl*-1 : 2 : 3-*benztriazole*, m. p. 178°, is obtained; the *base* resulting from its hydrolysis has m. p. 151°. By treatment with nitric acid, D 1·52, the acetyl derivative yields 4-*chloro*-5-*acetylamino*-1-p-*nitrophenyl*-1 : 2 : 3-*benztriazole*, m. p. 265°. The corresponding *base*, m. p. above 300°, orange-yellow needles, is reduced by stannous chloride and acetic acid to 4-*chloro*-5-*amino*-1-p-*aminophenyl*-1 : 2 : 3-*benztriazole*, m. p. 234°, the exhaustive chlorination of which in acetic and concentrated hydrochloric acids yields a *substance*, $C_{12}H_3O_2N_3Cl_8$, m. p. 180° (decomp.), white prisms, which is also produced by the exhaustive chlorination of 5-amino-1-*p*-aminophenyl-1 : 2 : 3-benztriazole, and receives the annexed formula because it yields 4 : 6 : 3′ : 5′-*tetrachloro*-5 : 4′-*dihydroxy*-1-*phenyl*-1 : 2 : 3-*benztriazole*, $OH{\cdot}C_6H_2Cl_2{\cdot}N\overset{N:N}{\diagup\!\!\!-\!\!\!-\!\!\!\diagdown}C_6HCl_2{\cdot}OH$, m. p. 234° (*acetyl* derivative, m. p. 260°), by reduction with stannous chloride and boiling glacial acetic acid.



By diazotising 5-amino-1-phenyl-1 : 2 : 3-benztriazole in concentrated sulphuric acid and heating the diluted solution, 5-*hydroxy*-1-*phenyl*-1 : 2 : 3-*benztriazole*, $C_{12}H_9ON_2$, m. p. 220° (*acetyl* derivative, m. p. 132°), is obtained. By chlorination in acetic acid, it yields, firstly 4-*chloro*-5-*hydroxy*-1-*phenyl*-1 : 2 : 3-*benztriazole*, m. p. 205° (*acetyl* derivative, m. p. 175°), and then 4 : 4-*dichloro*-5-*keto*-1-*phenyl*-4 : 5-*dihydro*-1 : 2 : 3-*benztriazole*, $N\!\!<\!\!\begin{array}{l}N\!-\!\!-\!C{\cdot}CCl_2{\cdot}CO\\ \qquad\ \ \| \qquad\quad\ \ |\\ NPh{\cdot}C{\cdot}CH\!=\!CH\end{array}$, m. p. 128° (rapidly

heated) or 187° (slowly heated); by reduction, the latter is converted into the former.

The bromination of 5-hydroxy-1-phenyl-1 : 2 : 3-benztriazole in glacial acetic acid yields 4-*bromo*-5-*hydroxy*-1-*phenyl*-1 : 2 : 3-*benztriazole*, m. p. 222° (decomp.), together with a small quantity of the keto-bromide.

4-*Bromo*-4-*nitro*-5-*keto*-1-*phenyl*-4 : 5-*dihydro*-1 : 2 : 3-*benztriazole*, obtained by shaking a chloroform solution of the preceding bromo-compound with nitric acid, D 1·52, decomposes at 100° or in boiling benzene, and yields 4 : 5-*diketo*-1-*phenyl*-4 : 5-*dihydro*-1 : 2 : 3-*benztriazole*, $NPh<\overset{N:N}{\text{———}}>C_6H_2O_2$, decomp. 170°, orange-red needles, which is converted into the *diazine*, $C_{18}H_{11}N_5$, m. p. 250°, yellow needles, by *o*-phenylenediamine in glacial acetic acid, and into 4 : 5-*dihydroxy*-1-*phenyl*-1 : 2 : 3-*benztriazole*, m. p. 214°, by sodium hydrogen sulphite and acetic acid.

[With K. Noll.]—3 : 5-Dinitro-*p*-xylene-2-diazoperbromide (Zincke and Ellenberger, Abstr., 1905, i, 486) is converted by sunlight, and more rapidly by heat, into 2-*bromo*-3 : 5-*dinitro*-p-*xylene*, m. p. 117°, and by aqueous ammonia at 0° into 3 : 5-*dinitro*-p-*xylyl*-2-*azoimide*, $C_6HMe_2(NO_2)_2\cdot N_3$, m. p. 71—73°, which yields 5-*nitro*-2 : 3-*dinitroso*-p-*xylene*, m. p. 81°, by heating at 105—130°, and 5-*nitro*-2 : 3-*diamino*-p-*xylene*, m. p. 169°, red needles, by reduction by alcoholic sodium sulphide. The diamine yields 6-*nitro*-4 : 7-*dimethylbenziminoazole*, $CH<\begin{smallmatrix}NH\\N\end{smallmatrix}>C_6HMe_2\cdot NO_2$, m. p. 221°, by boiling with formic acid, and 5-*nitro*-4 : 7-*dimethyl*-1 : 2 : 3-*benztriazole*, $N<\begin{smallmatrix}N\\NH\end{smallmatrix}>C_6HMe_2\cdot NO_2$, m. p. above 300°, by treatment with sodium nitrite and hydrochloric acid in boiling alcoholic solution. The latter is reduced by tin and hydrochloric acid to 5-*amino*-4 : 7-*dimethyl*-1 : 2 : 3-*benztriazole*, m. p. 224° (*acetyl* derivative, m. p. above 300°), which yields, after diazotisation and heating of the solution, 5-*hydroxy*-4 : 7-*dimethyl*-1 : 2 : 3-*benztriazole*, m. p. 240°, which does not couple with diazonium salts, forms an *acetyl* derivative, m. p. 211°, and is converted by nitric acid, D 1·52, at 0° into 4-*nitro*-5-*keto*-4 : 7-*dimethyl*-4 : 5-*dihydro*-1 : 2 : 3-*benztriazole*, $N<\begin{smallmatrix}N-C\cdot CMe(NO_2)\cdot CO\\ NH\cdot C\cdot CMe=\!=\!=CH\end{smallmatrix}$, m. p. 138° (decomp.). This quinonitrole is converted by boiling glacial acetic acid into 4-*hydroxy*-5-*keto*-4 : 7-*dimethyl*-4 : 5-*dihydro*-1 : 2 : 3-*benztriazole*, m. p. 150° (decomp.). By chlorination in acetic acid, 5-hydroxy-4 : 7-dimethyl-1 : 2 : 3-benztriazole yields 4-*chloro*-5-*keto*-4 : 7-*dimethyl*-4 : 5-*dihydro*-1 : 2 : 3-*benztriazole*, m. p. 170° (decomp.).

4 : 6 : 6 : 7-*Tetrachloro*-5-*keto*-4 : 7-*dimethyl*-4 : 5 : 6 : 7-*tetrahydro*-1 : 2 : 3-*benztriazole*, $N<\begin{smallmatrix}N-C\cdot CMeCl\cdot CO\\ NH\cdot C\cdot CMeCl\cdot CCl_2\end{smallmatrix}$, m. p. 175° (decomp.), obtained by saturating with chlorine a suspension of 5-amino-4 : 7-dimethyl-1 : 2 : 3-benztriazole in cold acetic and concentrated hydrochloric acids, is reduced by stannous chloride and hydrochloric acid to 6-*chloro*-5-*hydroxy*-4 : 7-*dimethyl*-1 : 2 : 3-*benztriazole*, m. p. 290° (decomp.) (*acetyl* derivative, m. p. 234°), which yields, not an ortho-

quinone, but an unexamined quinonitrole by oxidation with nitric acid.

[With J. KOHLHAAS.]—The following results show that coumaranone derivatives behave like benzenoid substances. The lactone of 2 : 4-dihydroxytriphenylacetic acid yields by chlorination or bromination in glacial acetic acid the *lactones* of 5-*chloro*-2 : 4-*dihydroxytriphenylacetic acid*, $OH\cdot C_6H_2Cl<\genfrac{}{}{0pt}{}{CPh_2}{O}>CO$, m. p. 147°, of 3 : 5-*dibromo*-2 : 4-*dihydroxytriphenylacetic acid*, $OH\cdot C_6HBr_2<\genfrac{}{}{0pt}{}{CPh_2}{O}>CO$, m. p. 164°, and of the corresponding bromo-compounds, $C_{20}H_{13}O_3Br$, m. p. 186°, and $C_{20}H_{12}O_3Br_2$, m. p. 186°. By exhaustive chlorination in glacial acetic acid, the lactone of 2 : 4-dihydroxytriphenylacetic acid yields the *pentachloro*-compound, $CO<\begin{array}{l}CPh_2\cdot C\cdot CHCl\cdot CCl_2\\ O——C—CCl_2\cdot CO\end{array}$, m. p. 207—209° (decomp.), which is converted into the preceding dichlorinated lactone by reduction with stannous chloride.

The nitration by acid, D 1·52, of the lactone of 2 : 4-dihydroxytriphenylacetic acid in cold glacial acetic acid yields the *lactones* of 5-nitro-2 : 4-dihydroxytriphenylacetic acid, $NO_2\cdot C_6H_2(OH)<\genfrac{}{}{0pt}{}{CPh_2}{O}>CO$, m. p. 183° (*acetyl* derivative, m. p. 159°), and of 3-*nitro*-2 : 4-*dihydroxytriphenylacetic acid*, m. p. 147° (*acetyl* derivative, m. p. 190°). By nitration under similar conditions, the *lactones* of 5-*chloro*-3-*nitro*-2 : 4-*dihydroxytriphenylacetic acid*, m. p. 196° (decomp.), and of 5-*bromo*-3-*nitro*-2 : 4-*dihydroxytriphenylacetic acid*, m. p. 192°, have been obtained. The *lactones* of 5-*amino*-2 : 4-*dihydroxytriphenylacetic acid*, m. p. 281° (decomp.) (*diacetyl* derivative, m. p. 215° [decomp.]), of 3-*amino*-2 : 4-*dihydroxytriphenylacetic acid*, m. p. 208°, and of 5-*chloro*-3-*amino*-2 : 4-*dihydroxytriphenylacetic acid*, m. p. 181°, have been prepared by the reduction of the corresponding nitro-compounds.

The *lactone*, m. p. 206° (decomp.), of 3 : 3 : 6 : 6-*tetrachloro*-2-*hydroxy*-4 : 5-*diketo*-3 : 4 : 5 : 6-*tetrahydrotriphenylacetic acid*,

$$CO<\begin{array}{l}CPh_2\cdot C\cdot CCl_2\cdot CO\\ O——C\cdot CCl_2\cdot CO\end{array},$$

obtained by the thorough chlorination of a suspension of the lactone of 5-amino-2 : 4-dihydroxytriphenylacetic acid in acetic and hydrochloric acids, is reduced by stannous chloride and acetic acid to the *lactone*, m. p. 220° (decomp.), of 3 : 6-*dichloro*-2 : 4 : 5-*trihydroxytriphenylacetic acid*, which gives a blue coloration with alcoholic ferric chloride. The latter in cold acetic acid is converted by nitric acid, D 1·4, into the *quinone*, $CO<\begin{array}{l}CPh_2\cdot C:CCl\cdot CO\\ O——C:CCl\cdot CO\end{array}$, m. p. 245° (decomp.), red crystals.

The chlorination of the lactone of 3-amino-2 : 4-dihydroxytriphenylacetic acid under the same conditions as the preceding isomeride yields an (unexamined) keto-chloride, which by reduction by stannous chloride is converted into the *lactone* of 5 : 6-*dichloro*-2 : 3 : 4-*trihydroxytriphenylacetic acid*, $C_{20}H_{12}O_4Cl_2$, m. p. 212° (decomp.) (*diacetyl* derivative, m. p. 182° [decomp.]), which is oxidised by nitric acid to the

quinone, $CO<\begin{matrix} CPh_2\cdot C\cdot CCl\colon CCl_2 \\ O \text{———} C\cdot CO\text{—}CO \end{matrix}$, which crystallises from benzene in garnet-red needles, m. p. 194° (decomp.), containing 1 mol. C_6H_6.

C. S.

Action of Cyanuric Chloride on Magnesium Organic Compounds. ADRIANO OSTROGOVICH (*Chem. Zeit.*, 1912, 36, 738—739).—The interaction of cyanuric chloride and magnesium phenyl bromide in ethereal solution yields successively dichlorophenyltriazine, $C_3N_3Cl_2Ph$, which crystallises in prismatic needles, m. p. 119—120° (compare Elzanowski, *Diss.*, Freiburg, Switz.), and chlorodiphenyltriazine, $C_3N_3ClPh_2$, which forms small, concentrically-arranged, thin needles, m. p. 135—136° (compare Ephraim, Abstr., 1893, i, 735).

F. B.

The Degradation of Monosodium Urate Under the Influence of Radium Emanation-*D*. JOHANNES KERB and PAUL LAZARUS (*Biochem. Zeitsch.*, 1912, 42, 82—90).—It has been claimed by Gudzent that radium-*D* converts the urate into a more soluble substance. The authors could, however, find no difference in the behaviour of a suspension of the urate whether exposed or not exposed to radium, provided that other conditions of experiment were absolutely identical. The increase in the solubility of the suspension depends on other conditions, more especially on the sterility of the mixtures and the alkalinity of the glass of the vessels. When the solution is quite sterile and the material of the vessel is chemically inactive, the urate does not decompose, even in presence of large quantities of emanation-*D*. There is, however, a rapid degradation of the substance in the presence of moulds.

S. B. S.

The Colour and Absorption of the Dirosanilidines of β-Hydroxyacraldehyde and Formic Acid. FRITZ REITZENSTEIN and GOTTLIEB BÖNITSCH (*J. pr. Chem.*, 1912, [ii], 86, 1—58. Compare Abstr., 1907, i, 648, and following abstract).—In order to determine the influence of the group $\cdot CH\colon CH\cdot CH\colon$ on the colour of the triphenylmethane dyes, the authors have prepared a number of dirosanilidines of β-hydroxyacraldehyde having the formulæ:

(I.) $R\cdot C_6H_4\cdot NH\cdot CH\colon CH\cdot CH\colon N\cdot C_6H_4\cdot R$

(II.) $R\cdot C_6H_3Me\cdot NH\cdot CH\colon CH\cdot CH\colon N\cdot C_6H_3Me\cdot R$

by condensing the isomeric amino-derivatives of tetramethyl-*p*-diaminotriphenylmethane and tetramethyl-*p*-diaminodiphenyltolylmethane with the acetal of propargaldehyde, and spectrographically examined the dyes obtained from them by oxidation [$R = 4:4'$-tetramethyldiaminodiphenylmethyl, $\cdot CH(C_6H_4\cdot NMe_2)_2$].

It is found that the introduction of this group produces dyes of a green shade. The position of the absorption bands of the dyes in aqueous or alcoholic solution is tabulated.

The acetal of α-bromo-β-ethoxypropaldehyde, prepared by heating αβ-dibromopropaldehyde with 1% alcoholic hydrogen chloride, is a

colourless liquid, b. p. 106—112°/15 mm. (compare Fischer and Giebe Abstr., 1898, i, 167).

3″-*Amino*-4 : 4′-*tetramethyldiamino*-4″-*methyltriphenylmethane*,

$$C_{24}H_{29}N_3,$$

obtained by condensing tetramethyl-*p*-diaminobenzhydrol with *o*-toluidine by means of strong sulphuric acid, forms crystalline, stellar aggregates, and melts at 141° to a pale blue liquid.

When dissolved in dilute hydrochloric acid and the solution heated for one day with the acetal of propargaldehyde on the water-bath, 2″-amino-4 : 4′-tetramethyldiaminotriphenylmethane yields *β-hydroxyacraldehyde-2-dileucanilidine*,

$$CH{<}{\begin{matrix}CH{:}CR\\CH{\cdot}CH\end{matrix}}{>}C{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C{<}{\begin{matrix}CR{:}CH\\CH{\cdot}CH\end{matrix}}{>}CH,H_2O,$$

which forms a light yellow powder.

β-Hydroxyacraldehyde-3-*dileucanilidine*,

$$CH{<}{\begin{matrix}CR{:}CH\\CR{\cdot}CH\end{matrix}}{>}C{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C{<}{\begin{matrix}CH{\cdot}CR\\CH{:}CH\end{matrix}}{>}CH,H_2O,$$

prepared in a similar manner from 3″-amino-4 : 4′-tetramethyldiaminotriphenylmethane is a yellow powder, sintering at 105°, m. p. 135°; the *hydrochloride* and *platinichloride* are mentioned.

β-Hydroxyacraldehyde-4-*dileucanilidine* is obtained in an impure condition from 4″-amino-4 : 4′-tetramethyldiaminotriphenylmethane; the *picrate*, $C_{49}H_{54}N_6,C_6H_3O_7N_3$, forms light yellow crystals (decomp. 125°).

β-Hydroxyacraldehyde-5-*methyl*-4-*dileucotoluididine*,

$$CR{<}{\begin{matrix}CH{:}CMe\\CH{=}CH\end{matrix}}{>}C{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C{<}{\begin{matrix}CH{\cdot}CMe\\CH{-}CH\end{matrix}}{>}CR,H_2O,$$

prepared from 4″-amino-4 : 4′-tetramethyldiamino-3″-methyltriphenylmethane, is a yellow, crystalline powder (decomp. 115—120°); the *hydrochloride* is greyish-green.

β-Hydroxyacraldehyde-6-*methyl*-4-*dileucotoluididine*,

$$CR{<}{\begin{matrix}CMe{:}CH\\CH{-}CH\end{matrix}}{>}C{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C{<}{\begin{matrix}CH{:}CMe\\CH{-}CH\end{matrix}}{>}CR,H_2O,$$

from 4″-amino-4 : 4′-tetramethyldiamino-2″-methyltriphenylmethane, decomposes at 90°, m. p. 130°; the *picrate*, $C_{51}H_{58}N_6,C_6H_3O_7N_3$, has m. p. about 170°, with previous sintering at 92°.

β-Hydroxyacraldehyde-5-*methyl*-2-*dileucotoluididine*,

$$CMe{<}{\begin{matrix}CH{:}CR\\CH{\cdot}CH\end{matrix}}{>}C{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C{<}{\begin{matrix}CR{:}CH\\CH{:}CH\end{matrix}}{>}CMe,H_2O,$$

prepared from 6″-amino-4 : 4′-tetramethyldiamino-3″-methyltriphenylmethane, forms a light yellow powder, sintering at 85°, m. p. 120°.

β-Hydroxyacraldehyde-4-*methyl*-3-*leucotoluididine*,

$$CH{<}{\begin{matrix}CR{=}CH\\CH{\cdot}CMe\end{matrix}}{>}C{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}C{<}{\begin{matrix}CH{=}CR\\CMe{\cdot}CH\end{matrix}}{>}CH,H_2O,$$

forms a light yellowish-green powder, decomposing at 75°, m. p. 120°.

5″-Amino-4 : 4′-tetramethyldiamino-2″-methyltriphenylmethane combines with propargaldehyde in aqueous solution at a low temperature, yielding the light yellow *additive* compound (decomp. 177°),

$$CMe{<}{\begin{matrix}CR{:}CH\\CH{\cdot}CH\end{matrix}}{>}C{\cdot}NH{\cdot}CH(OH){\cdot}C{:}CH.$$

If the combination is effected in the presence of dilute hydrochloric acid, the *compound*,

$$CMe\lessdot\begin{matrix}CR:CH\\CH\cdot CH\end{matrix}\gtrdot C\cdot NH\cdot CH(OH)\cdot CHCl\cdot CH_2Cl,HCl,$$

is produced, which crystallises in slender, citron-yellow needles containing $2H_2O$ (decomp. 253°).

β-Hydroxyacraldehyde-4-leucodianilidine hydrochloride,

$$CR\lessdot\begin{matrix}CH:CH\\CH\cdot CH\end{matrix}\gtrdot C\cdot NH\cdot CH:CH\cdot CH:NPh,HCl,$$

prepared by the addition of 4 : 4′-tetramethyldiamino-4″-aminotriphenylmethane dissolved in alcoholic hydrogen chloride to an alcoholic solution of the additive compound of aniline and propargaldehyde, $NHPh\cdot CH(OH)\cdot C⋮CH$ (Claisen, Abstr., 1904, i, 14), forms bluish-green crystals, sintering at 155°, m. p. 178°.

β-Hydroxyacraldehyde-3-leucodianilidine hydrochloride,

$$CH\lessdot\begin{matrix}CR:CH\\CH\cdot CH\end{matrix}\gtrdot C\cdot NH\cdot CH:CH\cdot CH:NPh,HCl,2H_2O,$$

obtained in similar manner from 3″-amino-4 : 4′-tetramethyldiaminotriphenylmethane, has m. p. 192°, with previous sintering at 160°.

β-Hydroxyacraldehyde-6-methyl-3-leucodi-p-toluididine hydrochloride,

$$CMe\lessdot\begin{matrix}CH:CH\\CR\cdot CH\end{matrix}\gtrdot C\cdot NH\cdot CH:CH\cdot CH:N\cdot C_6H_4Me,HCl,H_2O,$$

prepared from 5″-amino-4 : 4′-tetramethyldiamino-2″-methyltriphenylmethane and the additive compound of *p*-toluidine and propargaldehyde, $C_6H_4Me\cdot NH\cdot CH(OH)\cdot C⋮CH$, is a yellow, crystalline substance, which darkens at 156° and has m. p. 180°.

When heated with aniline on the water-bath and the resulting product treated with dilute hydrochloric acid, the acetal of β-ethoxyacraldehyde yields the hydrochloride of β-hydroxyacraldehydedianilidine, $NHPh\cdot CH:CH\cdot CH:NPh,HCl$ (Claisen, *loc. cit.*).

β-Hydroxyacraldehyde-6-methyl-3-dileucotoluididine,

$$CMe\lessdot\begin{matrix}CR:CH\\CH\cdot CH\end{matrix}\gtrdot C\cdot NH\cdot CH:CH\cdot CH:N\cdot C\lessdot\begin{matrix}CH:CR\\CH\cdot CH\end{matrix}\gtrdot CMe,$$

prepared from 5″-amino-4 : 4′-tetramethyldiamino-2″-methyltriphenylmethane, is light yellow in colour, and has m. p. 194°. F. B.

Colour and Absorption of the Dirosanilidines of Formic Acid. Fritz Reitzenstein and Gottlieb Bönitsch (*J. pr. Chem.*, 1912, [ii], 86, 58—72).—A description of the preparation of compounds of the following formulæ, together with an account of the spectrographic examination of the dyes obtained from them by oxidation with chloroanil in glacial acetic acid solution :

(I.) $CH(C_6H_4\cdot NMe_2)_2\cdot C_6H_4\cdot NH\cdot CH:N\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2$.

(II.) $CH(C_6H_4\cdot NMe_2)_2\cdot C_6H_3Me\cdot N\cdot CH:N\cdot C_6H_3Me\cdot CH(C_6H_4\cdot NMe_2)_2$.

Di-*m*-tolylformamidine, prepared by heating *m*-toluidine with ethyl orthoformate, forms long, lustrous needles, m. p. 125° (compare Niementowski, Abstr., 1887, 935).

The condensation of ethyl orthoformate and 4″-amino-4 : 4′-tetramethyldiaminotriphenylmethane in boiling amyl ether solution gives rise to 4-*dileucoformanilidine* (formula I), m. p. 199—200°, whilst in 30% acetic acid solution a *hydrate*, $C_{47}H_{52}N_6,2H_2O$, m. p. 70°, is

produced. When dissolved in a mixture of alcohol and acetic acid, the formanilidine is oxidised by chloroanil to *p*-aminomalachite-green; in glacial acetic acid a blue dye is formed.

Diphenylformamidine condenses with tetramethyldi-*p*-aminobenzhydrol in the presence of concentrated sulphuric acid, yielding the *sulphate* of 4-dileucoformanilidine, $C_{44}H_{52}N_6,H_2SO_4$, which forms a very light, white powder, decomposing at 160°, m. p. 200°.

o-, *m*-, and *p*-Ditolylformamidines condense with tetramethyldi-*p*-aminobenzhydrol in dilute hydrochloric acid solution, yielding *compounds* of the formula $C_{24}H_{29}N_3$; of these, the ortho-compound is a white powder, m. p. 140°.

The condensation of *o*- and *p*-ditolylformamidines with tetramethyldi-*p*-aminobenzhydrol in the presence of strong sulphuric acid gives rise to compounds, $C_{49}H_{56}N_6$ (formula II above), of which the ortho-derivative, on oxidation with chloroanil in glacial acetic acid solution, yields a blue dye and the para-derivative a bluish-green. F. B.

Tetraformaltrisazine from Formaldehyde and Hydrazine Hydrate, a New Reducing Agent for Analytical Chemistry. KARL A. HOFMANN and DOUGLAS STORM (*Ber.*, 1912, 45, 1725—1730).—*Tetraformaltrisazine*, $\begin{matrix} NH\cdot CH_2\cdot N\cdot CH_2\cdot NH \\ | \quad\quad\quad | \quad\quad\quad | \\ NH\cdot CH_2\cdot N\cdot CH_2\cdot NH \end{matrix}$, which is readily prepared from formaldehyde and hydrazine hydrate, is a reducing agent free from alkali and acid, and milder in its action than hydrazine. It crystallises in lustrous, silky, flat needles, sometimes radially grouped, or long, doubly refractive plates pointed at the end; decomp. 225°. It tastes sweet.

The precipitate with mercuric chloride dries to a colourless powder, $C_4H_{12}N_6,3HgCl_2$. The precipitate with silver nitrate soon changes to a very fine mirror; palladium chloride behaves similarly; gold chloride is reduced to a blue colloid, which is subsequently precipitated as a dark powder. In alkaline solution copper salts are reduced to cuprous oxide, mercury, gold and silver salts to the metal, whilst platinum and palladium chlorides yield stable, deep reddish-brown solutions.

In presence of excess of sodium hydroxide, chromate, molybdate, vanadate, selenite, and tellurite remain unchanged even at 100°, but on addition of ammonium chloride, indigo-blue molybdenum oxide, red selenium, or black tellurium are precipitated.

The compound is very stable towards alkali, but readily decomposed by acids. Carbon dioxide eliminates hydrazine, leaving colourless, polymeric formalazine, $(CH_2N_2CH_2)_n$.

Tetraformaltrisazine contains only hydrazine nitrogen. Two of the hydrazine groups are more readily oxidised in alkaline solution than the third.

With benzaldehyde, benzylideneazine and polymeric formalazine are formed.

When formalazine is heated in an atmosphere of nitrogen at 300—400°, a yellow oil distils of objectionable odour. This spontaneously returns to formalazine even in alcoholic solution.

E. F. A.

Thiophenols II. *p*:*p*′-Azophenyl Methyl Sulphide and Its Derivatives. KURT BRAND and A. WIRSING (*Ber.*, 1912, 45, 1757—1771).—p:p′-*Azoxyphenyl methyl sulphide*, $ON_2(C_6H_4\cdot SMe)_2$, is obtained by the action of *p*-nitrophenyl methyl sulphide (Abstr., 1909, i, 855) on a boiling solution of sodium methoxide in methyl alcohol. It forms light yellow needles, m. p. 135—136°. By digestion on the water-bath for several hours with excess of methyl sulphate, removal of the excess by repeated evaporation with methyl alcohol and water, and precipitation of the aqueous solution with potassium iodide, it gives long, yellow needles, m. p. 130—132° (decomp.), of p:p′-*azoxyphenyldimethylsulphinium iodide*, $ON_2(C_6H_4\cdot SMe_2I)_2$.

p:p′-*Hydrazophenyl methyl sulphide*, $N_2H_2(C_6H_4\cdot SMe)_2$, is obtained by reducing *p*-nitrophenyl methyl sulphide with zinc dust and sodium hydroxide in alcoholic solution. When pure, it forms colourless crystals, m. p. 104°; it is oxidised to the azo-compound when air is passed through the alcoholic solution. Treatment with concentrated hydrochloric acid does not give rise to a semidine transformation, but produces *p*-aminophenyl methyl sulphide hydrochloride (Abstr., 1911, i, 39, 285), the oxygen thereby becoming available forming *p*:*p*′-azophenyl methyl sulphide and other oxidation products.

p:p′-*Azophenyl methyl sulphide*, $N_2(C_6H_4\cdot SMe)_2$, is prepared by reducing *p*-nitrophenyl methyl sulphide with zinc dust and sodium hydroxide, and oxidising the filtered solution by passing air through it. It forms yellowish-red leaflets, and has m. p. 177—178°. With concentrated mineral acids and strong organic acids, it gives deep blue solutions; the formation of this colour is a very delicate test for traces of the compound. When dry hydrogen chloride is led into a chloroform solution, blue needles, with a metallic glance, of p:p′-*azophenyl methyl sulphide hydrochloride* are precipitated, but they lose hydrogen chloride even on filtering.

p:p′-*Azophenyl methyl sulphide sulphate*, $C_{14}H_{14}N_2S_2,2H_2SO_4$, is obtained as shining, green needles, when a solution of the sulphide in glacial acetic acid is precipitated with concentrated sulphuric acid. The *trichloroacetate*, $C_{14}H_{14}N_2S_2,2CCl_3\cdot CO_2H$, is produced by mixing chloroform solutions of the sulphide and trichloroacetic acid; it forms green, shining needles, possessing a strong metallic glance. Cryoscopic measurements in trichloroacetic acid as solvent indicate that the salt is unimolecular.

The following *double* salts have also been obtained:

$$C_{14}H_{14}N_2S_2,HCl,HgCl_2,$$

indigo-blue crystals; $C_{14}H_{14}N_2S_2,HCl,FeCl_3$, green leaflets;

$$(C_{14}H_{14}N_2S_2,HCl)_2,FeCl_3,$$

bluish-violet needles having a green shimmer; $C_{14}H_{14}N_2S_2,HCl,SnCl_4$, green leaflets. They were prepared by the action of *p*:*p*′-azophenyl methyl sulphide with the metallic chloride in glacial acetic acid solution, the addition of hydrochloric acid being necessary in the case of the first and third salt.

p:p′-*Azophenyldimethylsulphinium methyl sulphate*,

$$N_2(C_6H_4\cdot SMe_2\cdot O\cdot SO_3Me)_2,$$

is obtained by digesting azophenyl methyl sulphide with excess of methyl sulphate on the water-bath until the blue colour changes to

red and the product is completely soluble in water. It forms thick, red crystals, which commence to decompose at 170°, and blacken at 185—190°. When the aqueous solution is treated with potassium iodide, slender, yellowish-red needles of p : p′-*azophenyldimethylsulphinium iodide*, $N_2(C_6H_4 \cdot SMe_2I)_2$, are obtained, m. p. 174—175°. The corresponding *sulphinium bromide*, $N_2(C_6H_4 \cdot SMe_2Br)_2$, forms yellowish-brown needles, and has m. p. 174°. The chloride could only be obtained in solution.

The blue colour produced when *p* : *p′*-azophenyl methyl sulphide is treated with acids is ascribed to the formation of a quinonoid isomeride, the hydrochloride, for example, being

$$SMeCl{:}C_6H_4{:}N \cdot NH \cdot C_6H_4 \cdot SMe$$

(compare Hantzsch, Abstr., 1908, i, 469, 484). In the case of the trichloroacetate and sulphate, the one molecule of acid is concerned in the formation of the quinonoid form, the other in salt formation, thus: $SMe(O_2C \cdot CCl_3){:}C_6H_4{:}N \cdot NH \cdot C_6H_4 \cdot \overset{H}{\underset{O_2C \cdot CCl_3}{S}} \cdot Me$. Similar considerations hold for the formulation of the double salts. T. S. P.

New Azo-colouring Matters from Aminodiphenylene Oxide. Alphonse Mailhe (*Compt. rend.*, 1912, 154, 1815—1817).—Nitrodiphenylene oxide is readily reduced by iron and hydrochloric acid to the corresponding amine, which is easily diazotised. The diazonium salts can very readily be coupled with amines and phenols, giving azo-dyes (compare Borsche and Bothe, Abstr., 1908, i, 528).

With aniline, the diazonium chloride yields *anilineazodiphenylene oxide*, $O<\begin{matrix}C_6H_4\\ C_6H_3N{:}N \cdot C_6H_4 \cdot NH_2\end{matrix}$, yellow crystals, m. p. 93°, giving a red solution in acids, which dyes silk orange-yellow. Other such azo-compounds have been prepared by coupling with *m*-toluidine, dimethylaniline, diphenylamine, and α- and β-naphthylamine. They are mostly yellow in colour, and in the case of the last three, the azo-compounds when in solution are turned deep blue by mineral acids.

Diphenylene oxide diazonium chloride has also been coupled up with a number of phenols, the following azo-compounds having been obtained: $O<\begin{matrix}C_6H_4\\ C_6H_3N{:}N \cdot C_{10}H_6 \cdot OH(\beta)\end{matrix}$, a brown powder, m. p. 95°.

$O<\begin{matrix}C_6H_4\\ C_6H_3N{:}N \cdot C_{10}H_4<\begin{matrix}(SO_3H)_2[6:8]\\ OH \quad [2]\end{matrix}\end{matrix}$, which gives a red solution in alcohol and presents a different absorption spectrum to the corresponding benzene azo-compound.

$O<\begin{matrix}C_6H_4\\ C_6H_3N{:}N \cdot C_{10}H_5<\begin{matrix}SO_3H[8]\\ OH \quad [2]\end{matrix}\end{matrix}$, orange-red crystals, which in an acid medium dye silk orange-yellow.

$O<\begin{matrix}C_6H_4\\ C_6H_3N{:}N \cdot C_{10}H_4<\begin{matrix}(SO_3H)_2[3:6]\\ OH \quad [2]\end{matrix}\end{matrix}$, a scarlet dye, which on silk

dyes a bright red. Its solution is turned carmine by sulphuric acid. It shows a remarkable absorption spectrum. All the rays above 0.580μ being absorbed.

By coupling with salicylic acid, an azo-*compound* is obtained, furnishing yellow crystals, which, when mordanted with chromium, dye an orange-yellow.

The above azo-compounds differ from the corresponding benzeneazo-compounds in their absorption spectra, and in that they possess brighter colours. W. G.

The Production of Carbamide by Hydrolysis of Proteins. ROBERT FOSSE (*Compt. rend.*, 1912, **154**, 1819—1821).—Proteins are hydrolysed by aqueous solutions of potassium, sodium or barium hydroxide, or potassium or sodium carbonate, and even by a suspension of pure slaked lime in water, carbamide being one of the products. Water, alone or acidified with acetic acid, does not produce this result. The quantity of carbamide produced from gelatin and a boiling solution of potassium hydroxide increases at first very rapidly, attains a maximum, and then slowly decreases. W. G.

Changes in the Physical Conditions of Colloids. XIII. The Relationship of Albumin to Inorganic Colloids and to the Salts of the Heavy Metals. WOLFGANG PAULI and LEO FLECKER (*Biochem. Zeitsch.*, 1912, **41**, 461—512. Compare Abstr., 1909, i, 618; 1910, i, 344).—For the purpose of the experiments, ox-serum albumin which had been submitted to a dialysis against distilled water lasting eight weeks, and the following inorganic colloids were employed: Ferric hydroxide, chromic hydroxide (positive colloids), and the sulphides of arsenic, antimony, copper, cadmium, and gold, and tungstic and molybdic acids (negative colloids). It was found that the suspensoids (colloids precipitated by small quantities of salts), as contrasted with the lyocolloids (colloids requiring larger concentrations of salts for precipitation), show no inhibition of precipitation of proteins when present in excess, and electrolytes invariably inhibit the precipitation of the protein-colloid complex. The protein precipitates by lyocolloids, on the other hand, are soluble in excess of the colloid, and in presence of excess of a lyocolloid, the presence of neutral salts favours the precipitation, and alkalis favour the precipitation when positive lyocolloids are present, acids favouring precipitation in the presence of the negative hyocolloids. Only when the protein is in excess do electrolytes inhibit the precipitation in the presence of lyocolloids, whereas under all conditions in the mixtures of suspenoids and proteins, they exert an inhibitory action on the precipitation. The precipitate of a suspensoid in the presence of protein contains only a fraction of the protein, whereas the precipitate in the presence of a lyocolloid contains the greater part, if not the whole, of the protein. The difference between the lyophobe suspensoids and the lyocolloids depends on the fact that the former are not stable unless minute quantities of electrolyte are present, for on prolonged dialysis they are precipitated. When brought into contact with protein free from electrolytes, the protein takes up the electrolytes, and produces an irreversible precipitate of the suspensoid. If

salts are present in the system, these will form adsorption compounds with the protein, and the latter will, therefore, not so readily adsorb the electrolytes from the suspensoid, which render the latter stable; hence, the inhibitory action of the salts on the precipitation of suspensoids by protein. The protective action of salts is, however, greater than that which can be accounted for by the above explanation. The authors explain this phenomenon on the assumption that the protein enters into combination with the salt in the method already postulated in Pauli's former papers, and yields a stable complex of colloid-protein-salt. The relationships between lyocolloids and proteins are the same as those between any two colloids of opposite charges, the complex formed taking the charge of that substance which is in excess. In this connexion it must be remembered that the protein can function both as an acid and a base.

The precipitation of proteins by salts of heavy metals was also investigated. This phenomenon belongs to the group of irregular series ("unregelmässige Reihen"). If the protein be mixed with the salt in low concentrations, a precipitate is formed. In higher concentrations, the mixture remains clear over a certain zône, with the re-formation of a precipitate when the concentration reaches still higher limits. The precipitation in the lower limits of salt concentration is explained on the assumption that the salt undergoes hydrolytic dissociation, and that the metallic oxide enters into combination with the protein, owing to the fact that the acidic functions of the latter are stronger than the basic functions. In this case, the anion of the salt can be detected in the dialysate of the complex. The metallic salts thus formed are assumed to be internal anhydrides. If, however, excess of the metal is present, another complex is formed, with the production of an electrically charged protein complex, the formation of which may be represented as follows (in the case of the iron compounds): $(x\mathrm{Fe(OH)_3}\,.\,\mathrm{Protein}) + y\mathrm{FeCl_3} = x(\mathrm{Fe(OH_3)}\,.\,\mathrm{Protein})\,y\mathrm{Fe}^{\cdot} + 3y\mathrm{Cl}'$. New coloured ions with positive charge are thus formed, the number of which is diminished by presence of excess of the metallic salt. According to Pauli's theory, the protein ions are heavily hydrated, and when these ions are present in the largest quantity, the viscosity of the mixture will attain a maximum. The measurement of viscosities over the zone of no-precipitation of ferric chloride-protein mixture reveals the presence of a mixture of maximum viscosity, which viscosity diminishes in mixtures containing larger quantities of metallic salt. The mixture with this maximum viscosity also shows the greatest amount of translation when placed in an electric field and investigated by the method of electrocataphoresis. It also shows the maximum diminution of electrolytic conductivity, and the absence of free Fe' ions in the mixture. The commencing point of reprecipitation in the highest zone is a function of the anion, the action of which is discussed by the authors. S. B. S.

The Nature of So-called Artificial Globulin. Robert Banks Gibson (*J. Biol. Chem.*, 1912, **12**, 61—64).—Moll's artificial serum-globulin is an intermediate step in the formation of alkali metaprotein. W. D. H.

Constitution of Hæmin. WILLIAM KÜSTER (*Ber.*, 1912, **45**, 1935—1946).—[With A. GREINER.]—The crude product obtained in the preparation of "hæmin" by Mörner's method is extracted with boiling benzene and then with chloroform at the ordinary temperature. The extracts are evaporated, leaving a residue consisting of *methylhaemin*, $C_{35}H_{34}O_4N_4ClFe$, large, brown rhombs, and a little dimethylhæmin. Methylhæmin is soluble in 0·2% sodium hydroxide and in hot aqueous sodium carbonate; during solution, the chlorine is displaced, although not quantitatively. The halogen is also removed by treatment with aniline, yielding *dehydrochloromethylhaemin*,

$$C_{35}H_{33}O_4N_4Fe,$$

an almost black powder, the solution of which in methyl alcohol and a few drops of dilute sulphuric acid yields the hæmin again by precipitation with hydrochloric acid. Dimethylhæmin is soluble in benzene, but is finally converted into an almost insoluble modification.

The methylation of acethæmin by Nencki's method yields methylhæmin, dimethylhæmin, and a *substance*, $C_{37}H_{39}O_4N_4Cl_2Fe$, m. p. 154—160°, which is apparently an additive compound of methyl chloride and dimethylhæmin.

[With P. DEIHLE].—Hæmatoporphyrin, prepared by the Nencki-Zaleski method, yields a *dimethyl* ester, $C_{36}H_{42}O_6N_4$, by treatment with alkali and methyl sulphate, but by repeated solution in acetone and precipitation by water, it is gradually converted into an *anhydro*-compound, $C_{34}H_{36}O_5N_4$, which is scarcely attacked by alkali and methyl sulphate, but is converted into a *dimethyl* ester, $C_{36}H_{40}O_5N_4$, by methyl alcohol and hydrogen chloride.

The product obtained by the action of hydrogen bromide in acetic acid on hæmin is converted by treatment with methyl alcoholic potassium hydroxide into a blackish-red, crystalline *substance* containing four methoxy-groups. Mesoporphyrin, obtained from acethæmin by Zaleski's hydrogen iodide process, is oxidised by chromic and sulphuric acids, yielding methylethylmaleimide and hæmatic acid.

The preceding experiments lead the author to the view that two of the nitrogen atoms in hæmin are basic, and are so related to the two carboxyl groups that one nitrogen is united with one carboxyl group as a betaine complex, the other nitrogen is united with the ferrichloride group, leaving one carboxyl group, which alone can be easily esterified. These views are developed to explain what occurs in the molecule when hæmin is converted into hæmatoporphyrin and into mesoporphyrin. C. S.

The Formation of Guanylic Acid from Yeast Nucleic Acid. WALTER JONES (*J. Biol. Chem.*, 1912, **12**, 31—35).—The methods at present in vogue for obtaining guanosine are difficult. In the present research an abundant yield was obtained by the action of pig's pancreas on yeast-nucleic acid. The digest was boiled, filtered, and treated at the boiling point with lead acetate. On cooling, the filtrate deposited a granular lead compound, which was filtered off, suspended in hot water, and decomposed with hydrogen sulphide. The filtrate from the lead sulphide was treated with potassium acetate

and poured into excess of alcohol. The precipitate so obtained was washed with alcohol and dried. It was purified by a repetition of the process, and was then found to possess the properties of the potassium salt of guanylic acid. The yield was 50% of the theoretical, and so large amounts are readily prepared. The active agent concerned in the reaction is destroyed by heat, and is more active at 40° than at 20°, but it is doubtful if it is a true catalyst, since a given amount of the pancreatic extract will decompose a given amount of yeast-nucleic acid and no more. It is suggested that the term *tetranuclease* should be given to it. It is probable that there are several tetranucleases, for this one has no action on thymus-nucleic acid. These two tetranucleotides also differ in their carbohydrate radicle: that in yeast-nucleic acid being *d*-ribose, that in thymus-nucleic acid being a hexose. W. D. H.

Digestion of Casein by Pepsin from the Calf, Pig, and Ox. W. VAN DAM (*Zeitsch. physiol. Chem.*, 1912, 79, 247—273. Compare Abstr., 1910, i, 290).—Recent literature concerning the identity of pepsin and chymosin is discussed critically. The digestion of casein by the stomach enzymes of pig, calf, and ox is studied in solutions of hydrochloric acid, sodium dihydrogen phosphate, mixtures of hydrochloric acid and also of acetic acid with sodium acetate; in short, in solutions of such hydrogen ion concentration that casein is not soluble in them. It is in all respects parallel to the rate of clotting. Thus in 0·3*N*-hydrogen chloride solution there is the same difference in the rate of digestion and clotting as in experiments by Mett's method. The products of digestion in strongly and weakly acid solutions are identical. There are no grounds for assuming the two enzymes are not the same. E. F. A.

Action of Trypsin. II. (a) The Influence of the Products of Hydrolysis on the Rate of Hydrolysis of Caseinogen by Trypsin. (b) The Autohydrolysis of the Caseinates. E. H. WALTERS (*J. Biol. Chem.*, 1912, 12, 42—54).—The products of the tryptic digestion of caseinogen have a slight impeding action on the velocity of the reaction, and this increases as the quantity of products increases. When a filtered solution of Grübler's trypsin is heated to 40°, a white, flocculent precipitate separates, and the filtrate from this contains the active hydrolysing agent. Neutral caseinogenates of lithium, sodium, and potassium in sterile solutions undergo autohydrolysis, 5% being hydrolysed in ninety-six hours at 57°. The basic caseinogenates undergo autohydrolysis rather more rapidly. The velocity constant for this change in the basic compounds of calcium and barium is about three times as great as that for the lithium and sodium compounds, indicating that some factor other than hydrogen or hydroxyl ions plays a part. Strong, but not weak, solutions of these salts have a slight tendency to coagulate after a long time. The velocity constant calculated from the unimolecular formula diminishes as the reaction proceeds, and this rapid falling off cannot be accounted for by the influence of the products of hydrolysis. The temperature-coefficient for the autohydrolysis of basic sodium caseinogenate between

37° and 73° is 7. The incomplete nature of autohydrolysis indicates that in the hydrolysis of caseinogen by trypsin (a unimolecular reaction) the position of equilibrium is shifted in the direction protein ⟶ products by the enzyme. W. D. H.

The Action of Proteolytic Enzymes on Clupein. F. Rogoziński (*Zeitsch. physiol. Chem.*, 1912, **79**, 398—414).—Trypsin, pancreatin, pancreatic fistula juice, and erepsin produce a rapid and extensive proteolysis of the clupein molecule, which is similar to that caused by boiling with mineral acids. Papain, β-lieno-protease (from spleen), and yeast juice act more feebly. The splenic enzyme is the strongest and yeast juice the weakest of the three. Pepsin-hydrochloric acid produces no recognisable effect on this protamine.

W. D. H.

Cleavage of Carbohydrates by Diastase. H. Bierry (*Bied. Zentr.*, 1912, **41**, 504; from *Bot. Centr.*, 1911, **117**, 568).—Certain diastases of mammals, such as amylase, maltase, and sucrase, require the presence of electrolytes, the electronegative ion having an especially important rôle. The original paper contains results of an investigation of ferments which cause the cleavage of hydrolysed sugars, with methods for collecting animal digestive liquids and for estimating the sugar in the digestive solutions. N. H. J. M.

The Condition of Malt Diastase after it has Acted. Henri van Laer (*Bull. Soc. chim. Belg.*, 1912, **26**, 223—226).—The peculiarities exhibited in a starch conversion by diastase are due to the adsorption compounds formed by the enzyme with the substrate and with the products of the reaction.

It is shown that diastase is recovered unaltered at the close of the reaction, and that it is just as active towards a second quantity of starch as an equal portion of fresh diastase, provided the temperature selected is one at which the enzyme is not destroyed. Diastase thus conforms strictly to Ostwald's definition of a catalyst. E. F. A.

The Synthesising and Hydrolysing Actions of Emulsin in Alcoholic Solution. Émile Bourquelot and Marc Bridel (*Compt. rend.*, 1912, **154**, 1737—1739, and *J. Pharm. Chim.*, 1912, [vii], **6**, 13—18. Compare Abstr., 1911, i, 1053; this vol., i, 522).—Emulsin acting on a solution of dextrose in 85% alcohol forms β-ethyl glucoside, which, on the other hand, it hydrolyses in aqueous solution. β-Ethyl glucoside, so prepared, is converted into its d-isomeride by the action of alcoholic hydrogen chloride. A similar synthesising action takes place with dextrose in other alcohols, giving the corresponding glucosides. This has been effected with methyl, propyl, and *iso*butyl alcohols.

When emulsin acts on a glucoside in alcoholic solution, the first effect is to hydrolyse the glucoside, and then the dextrose so formed unites with the alcohol to give an alkyl glucoside. W. G.

Organic Chemistry.

Action of Ozone on Organic Compounds. III. CARL D. HARRIES (*Annalen*, 1912, 390, 235—268).—The object of the present investigation is to explain the formation of ozonides containing an amount of oxygen greater than that corresponding with the degree of unsaturation of the organic compound. The author is of opinion that the ozonised oxygen produced by the silent discharge in a 10-tube ozoniser is a mixture of different modifications of oxygen, and contains oxozone, O_4, in addition to ozone. By treating the crude mixture with sodium hydroxide and with concentrated sulphuric acid, the oxozone is destroyed and the purified gas produces normal ozonides only.

[With FRITZ EVERS.]—Δ^{β}-Butylene is prepared from purified *sec.*-butyl alcohol by distillation with phosphoric oxide. It is shown to be free from isomerides, and consists probably almost entirely of the *cis*-modification; the presence of a little of the *trans*-form probably will not be of importance in the following experiments, because the ozonides of ethylenic stereoisomerides (for example, those of oleic and elaidic acids) scarcely differ in behaviour.

The butylene is ozonised by the Harries-Koetschau method; the methyl chloride used as solvent is specially treated to free it from unsaturated impurities. The ozonised oxygen contains 11—14% of "crude ozone." After being washed with 5% sodium hydroxide and with concentrated sulphuric acid, the gas contains 5·8—9·3% of "pure ozone." This mixture still contains moisture, which is removed by passing the gas through coils cooled by ether-carbon dioxide. By treatment with "pure" ozone, Δ^{β}-butylene gives, after the evaporation of the solvent, a 75% yield of a viscous oil, which is separated by distillation under reduced pressure into *butylene ozonide*, $O<\begin{matrix}O\cdot CHMe\\ | \\ O\cdot CHMe\end{matrix}$, b. p. 15—16°/20 mm., D_{22}^{22} 1·0217, n_D^{22} 1·38546, a colourless liquid having a stupefying odour and dissolving readily in water, and *bisbutylene ozonide*, $(C_4H_8O_3)_2$, an extremely viscous, almost odourless, non-volatile liquid, which explodes at about 125°.

By treatment with "crude" ozone in a similar manner, Δ^{β}-butylene gives an 86% yield of a viscous liquid which is separated by distillation under reduced pressure into impure *butylene oxozonide*, $C_4H_8O_4$, b. p. 20—22°/22 mm., D_{20}^{20} 1·0336, n_D^{20} 1·38404, and *bisbutylene oxozonide*, $(C_4H_8O_4)_2$, a viscous liquid having an odour of paraldehyde, exploding at 125°, and having D_{19}^{19} 1·1604 and n_D 1·43167.

By further treatment with "crude" ozone, butylene ozonide remains unchanged, whilst the bimolecular form is converted into bisbutylene oxozonide. By treatment with water, butylene oxozonide undergoes extensive decomposition at once, but the bimolecular form appears to change, at least in part, to the bimolecular form of the normal ozonide.

All four substances are decomposed by boiling water, yielding acetaldehyde, acetic acid, hydrogen peroxide, and oxygen. The rate

of the decomposition has been determined by estimating after definite intervals of time the amount of acetic acid and also the active oxygen by aqueous potassium iodide.

[With Erik Riedl von Riedenstein.]—The ozonisation of allylbenzene is effected in carbon tetrachloride. With "pure" ozone, the product is a viscous, malodorous liquid, which is separated by fractional distillation into *phenylallyl ozonide*, $O<\begin{matrix}O\cdot CH_2 \\ | \\ O\cdot CH\cdot CH_2Ph\end{matrix}$, b. p. 67—71°/0·4—0·8 mm., D_{21}^{21} 1·1362, n_α 1·51371, n_D^{21} 1·51761, n_γ 1·53722, a colourless, mobile liquid which explodes feebly when heated, and is much less odorous than the crude ozonide, and *bisphenylallyl ozonide*,

$$(C_9H_{10}O_3)_2,$$

a viscous, colourless, non-volatile liquid which explodes at 104—106°, and has D_{21}^{21} 1·1766 and n_D^{21} 1·54216. Both ozonides are only slightly attacked by boiling water, but are easily decomposed by hot glacial acetic acid, yielding thereby formaldehyde, phenylacetaldehyde and its peroxide, and phenylacetic acid.

When ozonised in hexane by "crude" ozone, allylbenzene yields an explosive white substance, which has absorbed considerably more oxygen than the compounds described previously; probably ozone has also entered the benzene nucleus, since the product of decomposition is a viscous, brown oil having powerful reducing properties.

Propenylbenzene in carbon tetrachloride yields with "pure" ozone a yellow oil, which rapidly decomposes with the formation of benzoic acid, and with "crude" ozone a viscous oil which also rapidly decomposes, but appears to contain an amount of oxygen greater than that corresponding with a mono-ozonide. The difference of behaviour of allylbenzene and propenylbenzene towards "pure" ozone is utilised to show that allylbenzene is converted into propenylbenzene by boiling alcoholic potassium hydroxide.

α-Methylstyrene, which is prepared best by heating phenyldimethylcarbinyl chloride and pyridine at 120°, is converted by "pure" ozone into an unstable *ozonide* (probably a mixture of the mono- and the bi-molecular normal ozonides), which decomposes in hot glacial acetic acid, yielding oxygen, formaldehyde, acetophenone, and a crystalline *substance*, m. p. 182—183°, which is assumed to be bimolecular acetophenone peroxide. C. S.

The Decomposition of Bromoform. George J. Sargent (*J. Physical Chem.*, 1912, 16, 407—420).—The experiments made by Gladstone and Tribe (1875) on the reduction of bromoform in alcoholic solution by the zinc-copper couple have been repeated.

The gaseous products are mainly methane and acetylene. The yield of acetylene rises from 13·5% to 22·3% as the concentration of the bromoform is increased from 1 : 4 to 4 : 5 of alcohol. When one part of water was added to the 1 : 4 solution, the yield of acetylene was 30·6% instead of 13·5%. It is suggested that the bromoform molecule is less protected by the solvent in presence of water in which it is less soluble. The addition of benzene instead of water does not materially increase the yield of acetylene.

The results are discussed in relation to the question of the con-

stitution of iron carbide in cast iron, etc. It is supposed that in the reduction of bromoform the radicle $CH\vdots$ is liberated and is either polymerised or reduced according to circumstances. Similarly, in the decomposition of iron carbide the radicle $CH_2\colon$ is liberated, and polymerises to ethylene, butylene, etc., or is reduced to ethane, etc.

It is therefore unnecessary to postulate the existence of a series of isomorphous iron carbides of general formula $(CFe_3)_n$ to account for the various hydrocarbons obtained (compare Campbell, Abstr., 1897, ii, 214). The same argument applies to uranium carbide and other carbides which yield a variety of gaseous products. R. J. C.

The Yield in the Grignard Reaction. PIERRE JOLIBOIS (*Compt. rend.*, 1912, **155**, 213—215).—In preparing magnesium ethyl iodide by the interaction of magnesium and ethyl iodide in dry ether, if the whole of the ethyl iodide is present at the start, a yield of about 41% is obtained, there being an evolution of ethane and ethylene (compare Cahours, *Annalen*, 1860, **114**, 240, and Löhr, Abstr., 1891, 682). If, on the other hand, the ethyl iodide is added drop by drop as the magnesium dissolves, the yield is 91%. The amount of Grignard reagent formed can be measured by titration with an ethereal solution of iodine: $MgEtI + 2I = MgI_2 + EtI$.

If to the Grignard reagent, carefully prepared and freed from ether, an excess of ethyl iodide is added, decomposition takes place according to the equation: $MgEtI + EtI = MgI_2 + C_2H_4 + C_2H_6$.

In the preparation of a magnesium alkyl iodide, it must not be left in contact with an excess of the alkyl iodide, and if it is required to use a known quantity, it is possible by means of the ethereal iodine solution to estimate the active magnesium. W. G.

Action of Hydrogen Peroxide on Glycerol. JEAN EFFRONT (*Bull. Soc. chim.*, 1912, [iv], **11**, 744—747).—When a mixture of hydrogen peroxide (10 volumes) with glycerol is distilled, with occasional fresh additions of hydrogen peroxide, the glycerol is quantitatively oxidised to two molecules of formic acid and one of carbon dioxide.

Examination of the liquid when the above oxidation has not been completed, demonstrates the presence of glyceric and glycollic acids as intermediate products.

Attention is drawn to the rather striking analogy between the action of hydrogen peroxide and of enzymes on proteins, amino-acids, etc. (compare Effront, this vol., i, 534). D. F. T.

Constitution of the Complex Metallic Salts of the Fatty Acids. J. V. DUBSKY (*Chem. Weekblad*, 1912, **9**, 562—564).—A review of earlier work on the complex metallic salts of the fatty acids, and a suggested graphic representation of the configuration of compounds of the type $[Me_3Ac_6]X_3$, in which Ac represents a fatty acid residue. A. J. W.

Ghedda or East Indian Wax. ANDREAS LIPP and EUGEN KUHN (*J. pr. Chem.*, 1912, [ii], **86**, 184—199).—The wax differs from ordinary beeswax in containing only one alcohol, namely, ceryl alcohol, which is present mainly in the form of esters.

It has m. p. 62—63°, acid value 5—7·5, ester value 86—92, and solidifies at 59—58°.

The alcohols and hydrocarbons present in the wax were isolated by hydrolysing it with alcoholic potassium hydroxide, neutralising the excess of alkali with hydrochloric acid, and fractionally extracting the solid, obtained by evaporation of the resulting solution, with light petroleum. The first three fractions yielded a mixture of ceryl alcohol and two hydrocarbons, $C_{26}H_{54}$ and $C_{30}H_{62}$, which crystallise in lustrous, silvery leaflets, m. p. 58° and 70° respectively, and are probably identical with the hydrocarbons (m. p. 59·5° and 68°) isolated from ordinary beeswax by Schwalb (Abstr., 1885, 962; 1887, 124). The remaining fractions yielded ceryl alcohol, which has m. p. 76°, and yields a *benzoyl* derivative crystallising in small, white needles, m. p. 53·5°.

The identity of the alcohol was established by its conversion into cerotic acid by heating it with soda-lime.

Cerotic acid has m. p. 77·5—78°; the methyl ester, m. p. 60°; the amide, m. p. 106°, and *anilide*, m. p. 97°, crystallise in slender, white needles (compare Marie, Abstr., 1896, 346). F. B.

The Properties of Phytin. M. A. JEGOROFF (*Biochem. Zeitsch.*, 1912, **42**, 432—439).—The author calls attention to the differences in the properties of various phytin preparations as regards their precipitability by molybdate solution. He confirms Starkenstein's results, which show that more substance is precipitated from a solution by molybdate after drying than before, and there is little difference in this respect whether the preparation is dried at the ordinary temperature in a vacuum or at 100°. The substance is more readily dried and loses more weight in an indifferent gas than in air. More precipitate is also obtained after treatment with hydrogen peroxide. The author has succeeded by means of dialysis in separating commercial phytin into three fractions, of which one is found in the dialysate, the second as an insoluble precipitate in the dialysor, and the third in solution in the dialysor. He criticises certain recent papers in which the existence of a phytase is claimed, and draws the conclusion that the existence of such an enzyme has not been proved. S. B. S.

Phytin and Phosphoric Acid Esters of Inositol. II. R. J. ANDERSON (*J. Biol. Chem.*, 1912, **12**, 97—113. Compare this vol., i, 607).—The following salts of phytic acid have been prepared:

Calcium magnesium potassium phytate, $C_6H_{12}O_{27}P_6Ca_3Mg_2K_2$, a colourless, amorphous powder.

Penta-calcium phytate, $C_6H_{14}O_{27}P_6Ca_5$, obtained by precipitating phytic acid with calcium acetate.

Tetra-calcium phytate, $C_6H_{16}O_{27}P_6Ca_4,12H_2O$, is a semicrystalline or granular powder.

Penta-magnesium phytate, $C_6H_{14}O_{27}P_6Mg_5,24H_2O$, is a crystalline powder.

Hexa-cupric phytate, $C_6H_{12}O_{27}P_6Cu_6$, formed on precipitating phytic acid with copper acetate.

Octa-silver phytate is an amorphous powder.

Hepta-silver phytate, $C_6H_{17}O_{27}P_6Ag_7$, is formed on precipitating the dilute nitric acid solution of the octa-silver phytate with alcohol.

On heating inositol with dry pyrophosphoric acid (3 mols.) at 200—220°, a *dipyrophosphoric ester* of inositol is obtained. To purify it, the mixture is boiled with dilute hydrochloric acid to transform pyrophosphoric acid into orthophosphoric acid, and the inositol derivative is then precipitated by the addition of barium chloride and a like volume of alcohol.

When inositol is heated with 6 mols. of pyrophosphoric acid, a *di-inositoltripyrophosphoric acid* is obtained. E. F. A.

Preparation of Acraldehyde. ALFRED WOHL and BRUNO MYLO (*Ber.*, 1912, **45**, 2046—2054).—The preparation of acraldehyde from glycerol by the use of potassium hydrogen sulphate or of other catalysts, namely, phosphoric or boric acid, or aluminium sulphate, gives very variable yields, and the product often contains besides acraldehyde, sulphurous acid and acetaldehyde.

The dehydration of glycerol can occur at the primary or the secondary alcoholic group, the final product in the first case being acetaldehyde, in the second acraldehyde:

$$\begin{array}{lll} OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH & \longrightarrow & OH\cdot CH_2\cdot C(OH){:}CH_2 \longleftrightarrow \\ \quad\downarrow & & OH\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow CH_2O + CH_3\cdot CHO \\ OH\cdot CH_2\cdot CH{:}CH\cdot OH & \longleftrightarrow & OH\cdot CH_2\cdot CH_2\cdot CHO \longrightarrow CH_2{:}CH\cdot CHO. \end{array}$$

In accordance with this explanation the preparation of acraldehyde should be favoured by a low temperature, since secondary hydroxyl groups dehydrate more readily than primary ones; it is actually shown that overheating favours the formation of acetaldehyde.

By starting with potassium hydrogen sulphate mixed with a comparatively small quantity of glycerol, and adding more glycerol gradually, a 60% yield of acraldehyde can be obtained, but the product contains 10% of sulphurous acid. Sulphates of aluminium (compare Senderens, Abstr., 1910, i, 649) and of other metals which can yield sulphuric acid at comparatively low temperatures behave similarly with glycerol. Sodium and potassium sulphates yield no acrolein.

On the other hand, the sulphates of the alkaline earths and the heavy metals cause a similar decomposition of glycerol, but the acraldehyde produced is free from sulphurous acid; magnesium sulphate is most effective, and easily yields 44% of a very pure product on a small scale; the catalytic effect of the other sulphates seems to fall in the order of the basicity of their oxides.

A special apparatus is described suitable for the production of large quantities of acraldehyde by the passage of glycerol vapour through an electrically heated vertical copper tube containing anhydrous magnesium sulphate as the catalytic agent, with subsequent fractional condensation of the issuing vapours. The apparatus, which yields a kilogram of pure acraldehyde in a day (yield 60% of the theoretical), is fully described in the original. D. F. T.

Action of Formaldehyde on Potassium Cyanide. HARTWIG FRANZEN (*J. pr. Chem.*, 1912, [ii], **86**, 133—149).—In order to obtain

experimental evidence in support of the view that the naturally-occurring amino-acids are formed in plants by the cyanohydrin reaction, the author has investigated the action of potassium cyanide on formaldehyde in aqueous solution. It was anticipated that the reaction of these substances would lead to the formation of glycollic, aminoacetic, glyceric, malic, and aspartic acids, but only the two first-named acids, together with iminodiacetic and nitrilotriacetic acids, could be isolated from the product.

With respect to the mechanism of the reaction, the author imagines that the potassium cyanide and formaldehyde react to form the compound $OK{\cdot}CH_2{\cdot}CN$, which is hydrolysed to $OH{\cdot}CH_2{\cdot}CN$, and finally to ammonia and glycollic acid; the nitriles of aminoacetic, iminodiacetic, and nitrilotriacetic acids are formed from these products as shown in the following scheme:

$$OH{\cdot}CH_2{\cdot}CN \xrightarrow{NH_3} NH_2{\cdot}CH_2{\cdot}CN \xrightarrow{OH{\cdot}CH_2{\cdot}CN} NH(CH_2{\cdot}CN)_2$$

and $N(CH_2{\cdot}CN)_3$.

For details of the separation of the acids the original should be consulted.

The *monosilver* salt of nitrilotriacetic acid, $C_6H_8O_6NAg$, crystallises in long, lustrous, colourless needles.

The *mercuric* salt of iminodiacetic acid, $C_4H_5O_2NHg$, forms a crystalline powder, consisting of very small leaflets. F. B.

New Transformations of Anhydrodextrose. EMIL FISCHER and KARL ZACH (*Ber.*, 1912, 45, 2068—2074. Compare this vol., i, 239).—The similarity of anhydrodextrose and dextrose in chemical behaviour extends to the effect of oxidation and reduction; the acid and alcohol obtained are named anhydrogluconic acid and anhydrosorbitol respectively, but it is not certain that the configuration of these two substances is identical with that of gluconic acid and sorbitol.

Anhydrosorbitol, $C_6H_{12}O_5$, is obtained by the reduction of anhydrodextrose in feebly alkaline aqueous solution by sodium amalgam; it forms colourless plates from alcohol, and needles from ethyl acetate, m. p. 113° (corr.), and tastes sweet at first, but afterwards slightly bitter; $[\alpha]_D^{20}$ $-7{\cdot}47°$ (in water). Except in m. p. and optical activity, anhydrosorbitol is very similar to the isomeric natural styracitol (Asahina, Abstr., 1909, i, 288).

Anhydrogluconic acid, $C_6H_{10}O_6$, is obtained by the oxidation of anhydrodextrose in aqueous solution by bromine; it is isolated as the *calcium* salt, which crystallises with $4H_2O$. The free acid crystallises in leaflets, m. p. 123—125° (corr.), which when exposed in a desiccator lose the elements of water, forming the *lactone*, $C_6H_8O_5$, which crystallises in cubes, m. p. 115° (corr.). The fresh solution of the latter in water is practically tasteless, but shortly becomes sour, probably giving an equilibrium mixture of lactone and free acid; the optical rotation shows a corresponding change from $[\alpha]_D^{20}$ $+82{\cdot}3°$ to $[\alpha]_D^{20}$ $+66{\cdot}4°$; by neutralisation of the aqueous solution, the *calcium*, *copper*, and *barium* salts of the acid were obtained.

An alcoholic solution of the lactone when saturated with ammonia deposits *anhydrogluconamide*, $C_6H_{11}O_5N$, needles, m. p. about 149° (decomp.); the amide gives a tasteless aqueous solution, which slowly undergoes hydrolysis, the change being accompanied by a fall in $[\alpha]_D^{20}$ from $+77·7°$ to $+52·8°$ in seven days.

From the easy formation of a lactone, the conclusion is drawn that anhydrogluconic acid contains a hydroxyl group in the γ-position to the carboxyl. Lack of material prevented any further investigation of the structure. D. F. T.

Dispersoid Chemistry of Cellulose. I. P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 41—43).—It has been found that colloidal solutions of cellulose can be obtained by the action of a large number of aqueous salt solutions on filter-paper or cotton-wool if the concentration, temperature, and pressure are suitably chosen. In general, the activity of a salt increases with its solubility and its capacity for combining with water, and for this reason, rise of temperature and pressure are favourable factors in many cases. In the case of saturated solutions of very soluble salts, the action takes place very rapidly at the ordinary boiling temperature.

Colloidal solutions containing about 1% of cellulose form solid jellies when cooled, and in many cases these exhibit a high degree of elasticity. H. M. D.

Acetolytic Degradation of Cellulose. Friedrich Klein (*Zeitsch. angew. Chem.*, 1912, 25, 1409—1415. Compare Skraup, Abstr., 1899, i, 852; Franchimont, 1900, i, 141; Skraup and König, Abstr., 1901, i, 370; Maquenne and Goodwin, Abstr., 1904, i, 799; Schliemann, Abstr., 1911, i, 179).—An exhaustive investigation of the action of acetic anhydride and sulphuric acid on cellulose. In the main, the results obtained are in accord with those of the earlier investigators, particularly those recorded by Schliemann (*loc. cit.*), except in that the formation of acetates of bioses other than cellobiose by the acetolysis of cellulose, regarded as probable by this investigator, was not observed.

It is established beyond dispute that at least one-third part of the monoses of cellulose are united as in cellobiose, for it is possible to obtain 30% of the theoretical yield of cellobiose octa-acetate from cellulose. The formation of cellobiose acetate is accompanied by that of cellulose-dextrin acetates soluble in alcohol, the specific rotatory powers of which increase from $+11°$ to about $+34°$ with a corresponding increase in the proportion of the acetyl radicle.

It is very probable that these substances are intermediate products in the degradation of cellulose to cellobiose, further hydrolysis of which does not, for an unknown reason, take place.

Other products of the acetolysis of cellulose are certain indefinite substances, soluble in water, which appear to be acetosulphates of cellobiose, dextrose, or some other degradation product of cellulose.

It is interesting to note that complete acetylation renders further

hydrolysis extremely difficult; for example, cellulose triacetate when acted on by a mixture of acetic anhydride (4 parts) and sulphuric acid (1 part) for seven days is converted mainly into esters soluble in water and only to the extent of 5% of the theoretical yield of cellobiose acetate. Cellulose-dextrin acetate, when treated similarly, yields products soluble in water, but no cellobiose acetate. It seems probable, therefore, that in the formation of cellobiose acetate, complete acetylation is preceded by hydrolysis or some other reaction, such as the ester-like union of sulphuric acid in the immediate neighbourhood of the oxygen-bridge linking, which is in this way kept open for subsequent hydrolytic attack. W. H. G.

Comparative Acetylation of Cellulose, Hydrocellulose, and Alkalised Cellulose. HERMANN OST and TOMIO KATAYAMA (*Zeitsch. angew. Chem.*, 1912, **25**, 1467—1470. Compare Ost, Abstr., 1911, i, 712; Klein, preceding abstract).—In order to obtain further knowledge of the differences between cellulose, hydrocellulose, and cellulose which has been treated with a 25% solution of sodium hydroxide at 110—120° for several hours ("alkalised" cellulose), the authors have studied the products obtained by treating these substances with a mixture of acetic anhydride, glacial acetic acid, and either sulphuric acid or zinc chloride. In all cases, the products obtained were found to have the composition corresponding with that of cellulose triacetate. Hydrocellulose, and more particularly alkalised cellulose, yield a greater proportion of acetates soluble in acetone than cellulose (cotton-wool) when similarly treated, the proportion of acetates soluble in acetone increasing in each case as the length of treatment with the acetylating mixture becomes greater.

It is remarkable that the highly polymerised cellulose triacetate soluble in chloroform, which forms an elastic, pliable film, has the same specific rotatory power ($-20{\cdot}5°$ to $-21°$) as the triacetate, which does not yield a coherent film. The acetates soluble in acetone derived from cotton wool and hydrocellulose have a specific rotatory power of $-17°$ to $-18°$, whilst the acetate soluble in acetone derived from alkalised cellulose is slightly more optically active, having $[\alpha]_D$ $-21{\cdot}9°$ (in chloroform).

Prolonged treatment of cellulose and hydrocellulose with the acetylating mixture leads to the formation of cellobiose octa-acetate, which, under suitable conditions, is converted into dextrose-α-penta-acetate. W. H. G.

A New Method of Isolating Betaine Hydrochloride from Molasses Residue. Separation of Glycine, Betaine, and Glutamic Acid. Absence of Betaine from the Fission Products of Certain Proteins. H. STOLTZENBERG (*Ber.*, 1912, **45**, 2248—2252).—Molasses residue contains alkali salts, carbohydrates, readily soluble non-saccharine matter, glutamic acid, and betaine. For the separation of betaine, the author proposes to take advantage of the fact that, whilst potassium chloride, glutamic acid hydrochloride, and betaine hydrochloride have closely similar solubilities in water, the

solubility of the two former in concentrated hydrochloric acid is very much less, whilst that of betaine hydrochloride is slightly greater than in pure water. The residues are therefore saturated with gaseous hydrogen chloride, the precipitate filtered, and the betaine hydrochloride isolated from the concentrated filtrate by means of alcohol.

The utility of the above solubility determinations in the investigation of the presence of betaine among the products of hydrolysis of proteins by hydrochloric acid was also investigated. From a mixture of glycine, betaine hydrochloride, and glutamic acid hydrochloride, the latter was deposited in 76% yield after saturation of the aqueous solution with hydrogen chloride. The filtrate, on concentration and treatment with alcohol, deposited 62% of betaine hydrochloride, whilst, from the residue, 76% of the glycocoll was obtained in the form of glycine ester hydrochloride.

Betaine was not found by this method among the fission-products of silk, goose feathers, blood, and other proteins. H. W.

Composition and Properties of Glycine Picrate and the Separation of Glycine from Alanine. Phœbus A. Levene and Donald D. van Slyke (*J. Biol. Chem.*, 1912, **12**, 285—294).—Glycine picrate is composed of 2 mol.-weights of glycine and 1 of picric acid. It softens at 199—200°, and decomposes at 202°. It is very soluble in hot water, but at 0°, 100 c.c. dissolves only 1·7 grams.

To separate glycine from alanine, the mixture is dissolved in hot water containing more picric acid than is required to combine with the glycine. The solution is cooled to 0°, and glycine picrate crystallises out. The filtrate is then treated with sulphuric acid and freed from picric acid with ether. The sulphuric acid is precipitated by an equivalent of titrated barium hydroxide solution. The alanine is left as a residue when the filtrate from the barium sulphate is concentrated to dryness. This still contains a little glycine, but that in the form of picrate is 90% pure. W. D. H.

Picrolonates of the Monoamino-acids. Phœbus A. Levene and Donald D. van Slyke (*J. Biol. Chem.*, 1912, **12**, 127—139. Compare Abderhalden and Weil, this vol., i, 422).—The procedure adopted is as follows: The amino-acid and picrolonic acid in molecular proportions, or with amino-acid in excess, are dissolved in a minimum amount of boiling water. On cooling, the picrolonate crystallises. Only in the case of *d*-alanine, *dl*-serine, and *d*-glutamic acid was there a tendency to carry down an excess of picrolonic acid which is readily removed by means of ether. The salts show characteristic crystalline form, but they decompose when they meet. The picrolonates appear to give good results in separating phenylalanine from glutamic and aspartic acids.

dl-*Alanine picrolonate* forms long, slender crystals, m. p. 216° (decomp.).

dl-*Aspartic acid picrolonate* crystallises in long, slender prisms with square ends; it blackens at 130°.

dl-*Glutamic acid picrolonate* separates in very fine, short spindles, decomp. 184°.

d-*Glutamic acid picrolonate*, which is similar to the inactive salt, has $[\alpha]_D^{20}$ +8·5°.

Glycine picrolonate crystallises in very characteristic rhomboid prisms, m. p. 214—215° (decomp.).

d-iso*Leucine picrolonate* forms long, slender, six-sided crystals grouped in stars, m. p. about 170°, $[\alpha]_D^{20}$ +32·8°.

l-*Leucine picrolonate* softens at 145°, m. p. 150°, $[\alpha]_D^{20}$ +19·6°. The picrolonate of natural leucine is seen under the microscope to consist of a mixture of long, slender, and rhomboid crystals.

dl-Leucine picrolonate forms rosettes of six-sided crystals.

l-*Phenylalanine picrolonate* forms two types of crystals: long, slender rods clustered in stars, and short, rectangular prisms, m. p. 208° (decomp.). A 25% racemised sample had $[\alpha]_D^{20}$ +22·8°.

dl-*Phenylalanine picrolonate* consists entirely of short, rectangular prisms, m. p. 211—212°.

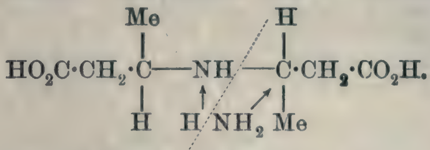
dl-*Serine picrolonate* crystallises in long, slender rods; it darkens above 200°.

Tyrosine picrolonate crystallises in rods grouped in rosettes, which blacken and sinter at 260°.

d-*Valine picrolonate* has m. p. 170—180°, $[\alpha]_D^{20}$ +23·4°. E. F. A.

The Mutual Relationship of the Optically Active Forms of ββ′-Iminodibutyric Acid and β-Aminobutyric Acid. HELMUTH SCHEIBLER (*Ber.*, 1912, 45, 2272—2297).—Under the action of ammonia, crotonic acid is converted into β-aminobutyric acid and ββ′-iminodibutyric acid. Prolonged heating has previously been shown to favour the production of the former at the expense of the latter acid. The author shows that an almost complete transformation of crotonic into β-aminobutyric acid can be achieved by prolonged heating of the former with ammonia, separation of the amino-acid formed, and subjection of the residue to a second treatment. Confirmation of the view put forward by Stadnikoff, that the formation of ββ′-iminodibutyric acid is due to the interaction of β-aminobutyric acid and crotonic acid is found in the production of this substance by the action of β-aminobutyric acid on barium crotonate. In order to decide in what manner the fission of ββ′-iminodibutyric acid occurs under the action of ammonia, the author has prepared the active ββ′-iminodibutyric acids. Synthetic ββ′-iminodibutyric acid consists of a mixture of the *meso*- and racemic forms, which can be separated by fractional crystallisation of the platinichlorides of their dimethyl esters from methyl alcohol. The racemic acid was resolved by fractional crystallisation of the brucine salt. *l*-ββ′-Iminodibutyric acid was transformed by ammonia into *l*-β-aminobutyric acid. Partial racemisation occurred at the same time, but not to a greater extent than when pure active β-aminobutyric acid was similarly treated. Hence it appears that the ammonia attaches itself to the imino-group in some manner, and that the C–N bond between the imino-group and one carbon skeleton becomes broken. The imino-group becomes converted into the amino-group. Substitution of an amino-group takes place in the other half of the molecule, probably without a Walden

inversion occurring, since the loss in activity can be explained on the ground of racemisation. The reaction may be represented thus:



The transformation of *l*-$\beta\beta'$-iminodibutyric acid into *l*-aminobutyric acid shows that the two halves of the imino-acid molecule possess the same configuration as the similarly active amino-acids. This follows also from the synthesis of the active imino- from active amino-acid, which was most readily performed by the union of methyl β-aminobutyrate with methyl crotonate. *d*-Methyl β-aminobutyrate and methyl crotonate yielded a mixture of *meso*-imino-ester and *d*-$\beta\beta'$-iminodibutyric ester. When inactive material was employed, the two inactive esters were not obtained in equal quantities, an excess of at least 6% of racemic ester pointing to an asymmetric synthesis.

The best conditions for the preparation of $\beta\beta'$-iminodibutyric acid and of β-aminobutyric acid respectively from crotonic acid and ammonia are fully described, as is the preparation of the former from β-aminobutyric acid and barium crotonate.

Methyl $\beta\beta'$-iminodibutyrate was used as starting point for the preparation of the active acid. After saponification by barium hydroxide and removal of barium, the acid was resolved by crystallisation of the *brucine* salt from alcohol, whereby *l-$\beta\beta'$-iminodibutyric acid* was obtained. The acids obtained from the mother liquor from the first crystallisation of the brucine salt contained the *meso*-acid, which was characterised by esterification of the acids by methyl alcohol and hydrogen chloride, and subsequent isolation of the *hydrochloride* of the *methyl* ester of meso-*$\beta\beta'$-iminodibutyrate*, m. p. 114—115° (corr.), and its *platinichloride*, m. p. 134—135°. The separation of *d*-iminodibutyric acid from the *meso*-acid can be effected by crystallisation of the platinichlorides of the methyl esters from methyl alcohol, in which that derived from the *d*-acid is the less soluble. The isolation of the *d*-acid from the mixture of acids obtained from the second mother liquor (see above) was effected by esterification and conversion into the platinichloride and crystallisation from methyl alcohol, whereby the *meso*-acid was removed. Removal of the racemic form was brought about by crystallisation of the methyl ester hydrochlorides from methyl acetate. The pure *d*-methyl ester hydrochloride, when hydrolysed with hydrochloric acid, yielded pure *d*-iminodibutyric acid. The latter could also be crystallised from its mixture with excess of the racemic acid after seeding with a crystal of the pure *d*-acid. At the same time a certain amount of resolution of the racemic acid by simple crystallisation occurred, since the yield of *d*-acid exceeded in amount that calculated from the activity of the mixture, and the mother liquors were lævorotatory. An attempt to resolve the syrupy racemic acid directly by this method was unsuccessful.

The racemic and *meso*-forms of $\beta\beta'$-iminodibutyric acid were similarly separated by crystallisation of the platinichlorides of their

methyl esters from methyl alcohol, the r-*compound*, m. p. 195—196°, being less soluble than the meso-*compound*, m. p. 134—135°.

r-*Methyl* $\beta\beta'$-*iminodibutyrate hydrochloride* has m. p. 142—143° (corr.). r-$\beta\beta'$-*Iminodibutyric acid* has m. p. about 158—160° (corr., decomp.), and could not be obtained in well-defined crystals.

meso-*Methyl* $\beta\beta'$-*iminodibutyrate hydrochloride* has m. p. 114—115° (corr.). The free *imino-acid* could not be obtained in the crystalline form. Its *hydrochloride* and *platinichloride* are crystalline.

l-$\beta\beta'$-*Iminodibutyric acid*, m. p. 179—180° (decomp.), has $[\alpha]_D^{20}$ $-65{\cdot}3°$ in aqueous solution, $[\alpha]_D^{20}$ $-56{\cdot}1°$ in *N*-hydrochloric acid solution. The *methyl* ester *hydrochloride*, m. p. 163—164° (corr.), has $[\alpha]_D^{20}$ $-42{\cdot}2°$ ($\pm 0{\cdot}4°$) in methyl-alcoholic solution. Its *methyl* ester *platinichloride*, has m. p. 200—201° (corr., decomp.).

d-$\beta\beta'$-*Iminodibutyric acid*, m. p. 179—180° (corr., decomp.), has $[\alpha]_D^{20}$ $+65{\cdot}5°$ in aqueous solution. Its *methyl* ester *hydrochloride*, m. p. 163—164° (corr.), has $[\alpha]_D^{20}$ $+42{\cdot}1°$ in methyl-alcoholic solution, and its *methyl* ester *platinichloride* has m. p. 200—201° (corr., decomp.).

l-$\beta\beta'$-Iminodibutyric acid was heated with aqueous ammonia at 110° during twenty hours, whereby it was converted into impure *l*-aminobutyric acid, $[\alpha]_D^{20}$ $-16{\cdot}2°$, which increased to $-20{\cdot}3°$ after recrystallisation from a mixture of methyl and ethyl alcohols. *d*-β-Aminobutyric acid, when similarly treated, decreased in activity from $+35{\cdot}3°$ to $+16{\cdot}5°$. *d*-$\beta\beta'$-Iminodibutyric acid, under similar treatment, yielded impure *d*-aminobutyric acid ($[\alpha]_D$ $+10{\cdot}6°$).

Active aminobutyric acids of the same sign as the imino-acid used were obtained when aqueous solutions of the active ammonium $\beta\beta'$-iminodibutyrates were heated under pressure. A solution of barium $\beta\beta'$-iminodibutyrate under similar conditions was decomposed into barium crotonate and ammonium crotonate.

Methyl crotonate and methyl β-aminobutyrate were maintained at 37° during several weeks. On distillation, methyl $\beta\beta'$-iminodibutyrate was obtained. The latter was converted into its platinichloride, which, by crystallisation from methyl alcohol, was separated into the platinichlorides of the *r*- and *meso*- esters. A similar experiment with methyl crotonate and methyl *d*-aminobutyrate showed that methyl *d*-$\beta\beta'$-iminodibutyrate and methyl *meso*-$\beta\beta'$-iminodibutyrate were formed. H. W.

Action of Bromine and Sodium Hydroxide on Carbamide and Guanidine Derivatives. I. VIKTOR VON CORDIER (*Monatsh.*, 1912, **33**, 759—796).—Arising out of the observation that monoacetylcarbamide when treated with sodium hypobromite in the Hüfner apparatus yields only one atom of nitrogen as gas (Abstr., 1908, ii, 983), the behaviour of a number of carbamide and guanidine derivatives towards sodium hypobromite has been studied.

The salts of carbamide and of guanidine with a variety of acids, like the free bases, all part with their nitrogen quantitatively.

Thiocarbamide and its derivatives either do not react at all or give very little nitrogen, but this influence is restricted to the thiocarbamide residue, and does not extend to a second carbamide or guanidine residue introduced as a substituent.

Bromine prevents the quantitative elimination of the nitrogen of the amino-group in which it has entered: this is exemplified by the behaviour of monobromoguanidine, which gives up only one nitrogen.

This applies equally to the acid groups $-CO{\cdot}CH_3$, $-CO{\cdot}C_6H_5$, $-CO{\cdot}NH_2$, all of which prevent the quantitative measurement of the nitrogen of the amino-group in question.

Phenyl and tolyl groups as in phenyl carbamide, phenylguanylthiocarbamide, phenylbiguanide, and ditolylcarbamide entirely prevent the elimination of nitrogen from the molecule.

An increase in the distance of the phenyl group from the amino-nitrogen as in benzylcarbamide overcomes the influence of the phenyl, as here both nitrogens are eliminated.

In the case of cyclic monoureides with bivalent acid esters, partial hydrolysis must be assumed, regenerating one amino-group. Parabanic acid and alloxan yield one atom; alloxantin yields two atoms of nitrogen. Veronal, which gives no nitrogen, affords an exception.

Mono- and especially cyclic diureides, for example, hydantoin and uric acid, give irregular results, which do not indicate any connexion between their constitution and the elimination of nitrogen.

The only faintly acid cyanogen group does not appear to hinder the elimination of nitrogen. The nitro-group behaves similarly in nitrocarbamide, nitrourethane, and nitroguanidine.

The methyl group sometimes hinders the elimination of nitrogen, as in methylguanidine nitrate, mono- and *s*-di-methylcarbamide; in other instances, it is without effect, for example, *as*-dimethylcarbamide and methylbiguanide.

The basic amino-group in semicarbazide does not hinder the nitrogen elimination, two atoms being liberated.

The method of elimination of nitrogen with sodium hypobromite can be used in such cases as glycine guanidine carbonate to determine whether or no an additive compound is present: five nitrogen atoms are here liberated. E. F. A.

Methylated Guanidines. II. MARTIN SCHENCK (*Arch. Pharm.*, 1912, 250, 306—329. Compare Abstr., 1911, i, 842).—Of the eleven theoretically possible methylated guanidines obtained by replacing successively the five hydrogen atoms of guanidine by methyl groups, only the three containing the group $NMe\colon C(NH_2){\cdot}N\colon$ have not been prepared; reactions which might be expected to produce these three actually result in the formation of substances containing $NH\colon C(NHMe){\cdot}N\colon$. The following new compounds are described: ββ-Dimethylguanidine forms an *aurichloride*, m. p. 248° (decomp.), *platinichloride*, decomp. 225°, and picrate, m. p. 230°, not 224°. *βββ′-Trimethylguanidine platinichloride* has m. p. 172—173°. *βββ′β′-Tetramethylguanidine*, $NH\colon C(NMe_2)_2$, obtained, ultimately in the form of the *aurichloride*, m. p. 142—144°, by the action of alcoholic ammonia on tetramethylthiocarbamide methiodide at 100° for nine hours, forms a *platinichloride*, which is extremely soluble in water, and a *picrate*, m. p. 130°. *αβββ′-Tetramethylguanidine*, $NMe\colon C(NHMe){\cdot}NMe_2$, obtained from αββ′-trimethyl-ψ-thiocarbamide and 33% alcoholic dimethylamine at the ordinary temperature or by heating αββ′-trimethyl-

ψ-thiocarbamide hydriodide or αβ′-dimethyl-β-ethyl-ψ-thiocarbamide hydriodide with alcoholic dimethylamine, forms an *aurichloride*, m. p. 115—117°, and a *picrate*, m. p. 158—160°. The action of methylamine on tetramethyl-ψ-thiocarbamide hydriodide results in the formation of, not a tetramethylated guanidine, but αββ′-trimethylguanidine and dimethylamine.

Pentamethylguanidine, $NMe{:}C(NMe_2)_2$, obtained by treating tetramethyl-ψ-thiocarbamide with 33% alcoholic dimethylamine at the ordinary temperature for fourteen days, forms an *aurichloride*, m. p. 130—132°, and *picrate*, m. p. 160—162°. C. S.

Pentamethylenedicarbimide. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1912, **45**, 2199—2200).—An ethereal solution of αε-di-iodopentane was added to a mixture of silver cyanate and sand. On gently warming, the ether was expelled and an energetic action then ensued, whereby *pentamethylenedicarbimide* was obtained in small quantity. It could not be obtained pure, since on keeping, more rapidly on warming, it became transformed into an amorphous insoluble mass, possibly the polymeric cyanurate. With fatty and fatty-aromatic alcohols and amines, it yielded compounds of low m. p. and small ability to crystallise. With purely aromatic phenols and amines, on the other hand, it yielded well-crystallised products of high m. p.; thus, *diphenylpentamethylenedicarbamide*, $CH_2(CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NHPh)_2$, has m. p. 202°, and the corresponding *derivative* from ethylaniline, m. p. 134°. Phenol and pentamethylenedicarbimide yield a *diphenyl urethane*, $CH_2(CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO_2Ph)_2$, m. p. 113—114°. H. W.

The Products of Explosion of Hydrogen Cyanide. G. SALOMONE (*Gazzetta*, 1912, **42**, i, 617—622).—An accidental explosion of 100 grams of anhydrous hydrogen cyanide led to the formation of white fumes with an odour of hydrocyanic acid, and of an amorphous, brown mass with an odour of bitter almonds. Heating this mass led to the evolution of hydrogen cyanide, and of ammonia and carbon monoxide at a higher temperature. The solid was a polymeride of hydrogen cyanide, and yielded small quantities of ammonium formate and formamide with water. Extraction with dry ether yielded a crystalline polymeride of cyanic acid, not identical with either cyamelide or cyanuric acid, having a molecular weight corresponding with the formula $C_5H_5O_5N_5$, and yielding a *potassium* salt, $C_5H_2O_5N_5K_3,6H_2O$, and a *silver* salt, $C_5H_2O_5N_5Ag_3,H_2O$. The pentacyanic acid had m. p. 148·5°. C. H. D.

Armstrong's Benzene Formula. HANS VON LIEBIG (*J. pr. Chem.*, 1912, [ii], **86**, 175—183).—A criticism of Armstrong's centric formula, together with an explanation of the difference in properties of benzene and *cyclo*octatetraene (Willstätter, this vol., i, 17), based on the author's hypothesis of the oscillatory nature of the double linking (Abstr., 1908, i, 445) and on the assumption that the carbon atoms of *cyclo* octatetraene are arranged in such a manner that the molecule contains four parallel double linkings. F. B.

Hydrogenation of Benzene. FRIEDRICH W. HINRICHSEN and RICHARD KEMPF (*Ber.*, 1912, **45**, 2106—2113).—Caoutchouc in

benzene is not attacked by hydrogen in the presence of platinum-black, but a large volume of hydrogen is absorbed, and *cyclo*hexane is formed. The platinum is not poisoned unless vulcanised caoutchouc has been employed. The same result is observed when benzene alone is used, and the rate of absorption of the hydrogen indicates that the hydrogenation of benzene to *cyclo*hexane is a reversible process.

When petroleum, b. p. 65—95°, is employed in the place of benzene, a considerable absorption of hydrogen is still observed, indicating the presence of unsaturated and of aromatic hydrocarbons. If the petroleum has been shaken with fuming sulphuric acid prior to use, a very much smaller absorption of hydrogen is observed. No further absorption of hydrogen occurs when caoutchouc is dissolved in petroleum which has been previously saturated with hydrogen in the presence of platinum-black.

*cyclo*Hexane is very conveniently separated from benzene by nitrating the latter and then fractionally distilling.

The presence of a trace of benzene in *cyclo*hexane is ingeniously detected as follows. The *cyclo*hexane (about 20 grams) is treated with a mixture of 41 c.c. of concentrated sulphuric acid and 36 c.c. of concentrated nitric acid. The temperature remains unchanged if the *cyclo*hexane is pure, but is raised 1° by the addition of even only 0·1 c.c. of benzene. C. S.

Syntheses in the Fatty Aromatic Series. V. ωω'-Diarylparaffins. Julius von Braun and H. Deutsch (*Ber.*, 1912, **45**, 2171—2188).—The action of sodium on fatty aromatic halogen compounds has been investigated. The reactivity of the latter appears to be largely independent of the molecular weight, and also of the nature of the halogen present. In all cases diarylparaffins are formed, the yield being apparently dependent on the number of methylene groups present in the original material: when this number is odd, diarylparaffins constitute the main product of the reaction (70—80%); when, however, the number is even, the yield of diarylparaffins is much lower (15—20% if ether is used as solvent). The secondary products consist of phenyl alkyl compounds without admixture of olefines.

Fully aromatic halogen compounds may be obtained in good yield by means of Grignard's reaction if the reagent is prepared at a low temperature and then treated with chloromethyl ether. From the ether thus obtained, the corresponding haloid can be made by treatment with halogen acid. Thus magnesium phenylpropyl bromide and chloromethyl ether yielded a mixture of propylbenzene, *phenylbutyl methyl ether*, b. p. 108°/11 mm. (above 45%), and αζ-diphenylhexane (12%). From the second compound, phenylbutyl bromide was obtained by treatment with fuming hydrobromic acid during five hours at 130—140°. Similarly, magnesium phenylamyl bromide and chloromethyl ether yielded *phenylhexyl methyl ether*, b. p. 140°/13 mm.

Phenylpropyl chloride, when treated with sodium, yielded propylbenzene and *αζ-diphenylhexane*, b. p. 206—208°/200 mm. The latter is a colourless, viscous liquid, which does not solidify at 0°. Phenylamyl chloride, under similar treatment, gave *n*-amylbenzene, b. p. 200—201°/745 mm., D_4^{20} 0·8662, n_D^{20} 1·4943, in 25% yield, and

$a\kappa$-diphenyldecane (compare Borsche and Wollemann, this vol., i, 24) in 75% yield. Similarly, from phenylheptyl chloride, *n*-heptylbenzene, b. p. 235°, D_4^{20} 0·8570, n_D^{20} 1·4865 (30%), and $a\chi$-*diphenyltetradecane*, b. p. 262—265°/8 mm. (70%), were prepared.

The products of the action of sodium on an ethereal solution of phenylhexyl chloride were hexylbenzene, b. p. 219—220°, D_4^{20} 0·8613, n_D^{20} 1·490 (yield above 85%), and $a\mu$-*diphenyldodecane*, b. p. 240°/20 mm. When ether was replaced by benzene, the yield of the latter compound was increased (up to 50%). Phenylbutyl chloride and sodium in ethereal solution yielded butylbenzene, b. p. 180—181°, D_4^{20} 0·8612, n_D^{20} 1·4936 (80%), and $a\theta$-*diphenyloctane*, b. p. 208—210°/8 mm. In benzene solution, better yields (up to 60%) of the latter compound were obtained. When sodium acted on phenylethyl chloride, ethylbenzene, b. p. 137°, and $a\delta$-diphenylbutane, m. p. 52°, were formed, together with a *product* of higher b. p., from which no definite substance could be isolated.

a-Phenyl-γ-xylylpropane, b. p. 202—206°/20 mm., was readily obtained by the condensation of phenylpropyl chloride and *o*-xylene in the presence of aluminium chloride. Similarly, phenylhexoyl chloride and toluene gave an 80% yield of *tolyl phenylamyl ketone*, b. p. 248—252°/14 mm., which yields oily condensation products with phenylhydrazine, hydroxylamine, and semicarbazide. In the toluene-half of the molecule, the carbonyl and methyl groups are in the para-position to one another, since the ketone is oxidised by dilute nitric acid with the formation of terephthalic acid. Reduction of the ketone by hydriodic acid, led to the formation of *a*-phenyl-*ζ*-*p*-tolylhexane.

Definite nitro- and sulphonic acid derivatives of the diarylparaffin could not be obtained. The action of oxalyl chloride on a solution of $a\theta$-diphenyloctane in carbon disulphide in the presence of aluminium chloride resulted in the isolation of the *dicarboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot[CH_2]_8\cdot C_6H_4\cdot CO_2H,$$

m. p. 245—250°, the *sodium* salt of which is sparingly soluble in water, whereas the *potassium* and *ammonium* salts dissolve readily. Oxidation of the acid by alkaline permanganate yielded terephthalic acid, which was quite free from phthalic acid. The acid was converted into its *ethyl* ester, m. p. 53—55°, by successive treatment with phosphorus pentachloride and ethyl alcohol, and into the corresponding *diamide*, m. p. 242°. Evidence was obtained to show that a certain quantity of the monocarboxylic acid was also formed during the action of oxalyl chloride on $a\theta$-diphenyloctane, but its isolation was not accomplished. In the diphenylpropane series, however, a derivative substituted in only one nucleus was readily obtained in the following manner: *o*-benzoylaminophenylpropyl chloride,

$$C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot[CH_2]_3\cdot Cl,$$

was condensed with benzene in the presence of aluminium chloride to o-*benzoylaminodiphenylpropane*, m. p. 207°, which was readily converted into the *hydrochloride* of o-*aminodiphenylpropane*, m. p. 205°. The free *base* has b. p. 208—212°/15 mm. It does not yield a crystalline picrate. Its *phenylthiocarbamide* derivative,

$$NHPh\cdot CS\cdot NH\cdot C_6H_4\cdot[CH_2]_3\cdot Ph,$$

has m. p. 132°. Its *benzylidene* derivative is an oil, whereas its

p-*nitrobenzylidene* derivative, $NO_2\cdot C_6H_4\cdot CH\colon N\cdot C_6H_4\cdot[CH_2]_3\cdot Ph$, has m. p. 59°. Diazotisation converted the amine into the corresponding *phenol*, b. p. 198—202°/15 mm. H. W.

Halogeno-salts of Tellurium [Tellurihalides]. ALEXANDER GUTBIER and FERDINAND FLURY [with C. EWALD] (*J. pr. Chem.*, 1912, [ii], 86, 150—166).—By methods similar to those previously described (Abstr., 1911, i, 182), the authors have prepared the telluribromides and tellurichlorides of ethylenediamine and a large number of aromatic amines. The chloro- and bromo-salts have the general composition, $(NHR_3)_2TeX_6$, and are respectively yellow and red in colour. Of the salts of aromatic amines, those of aniline, pyridine, and quinoline have been described by Lenher (Abstr., 1900, i, 379).

Ethylenediamine tellurichloride, $(C_2H_{10}N_2)TeCl_6$, crystallises in compact needles, the aniline salt in slender, felted needles, the *methylaniline* salt, $(NH_2MePh)_2TeCl_6$, in tabular, often scaly crystals, and the *dimethylaniline* salt in stout, fibrous crystals. The chloro-salt of *ethylaniline* forms soft leaflets, of *diethylaniline*, compact, parallel aggregates of very small platelets, often having an irregular hexagonal outline; the o- and p-*toluidine* salts form lath-like crystals, the m-*isomeride*, strongly refractive, stout crystals. Of the isomeric *xylidine tellurichlorides*, the *o*-4-compound crystallises in lustrous, elongated, pointed prisms, the *m*-4-compound in brownish-yellow platelets or needles, and the *p*-compound in lustrous platelets or laths. The pyridine salt, $(C_5H_5NH)_2TeCl_6$, crystallises in thin, hexagonal plates or laths, the 2-*methylpyridine* and quinoline salts in prisms; the *benzylamine* compound forms bright yellow aggregates of lamellar or prismatic crystals, the *benzylethylamine* salt, lustrous, stellar aggregates of prisms, and the α-*naphthylamine* salt, greenish-yellow needles.

Of the telluribromides, the *ethylenediamine* salt crystallises in glistening red needles, the *propylenediamine* salt, $(C_3H_{12}N_2)TeBr_6$, in lustrous, bright red platelets, the aniline salt in soft, microscopic, felted prisms, the *methylaniline* salt in lustrous, scaly platelets, the *dimethylaniline* salt in small, light red plates, the *ethylaniline* salt in glistening, brownish-red platelets, and the *diethylaniline* salt in glistening, rectangular crystals. The bromo-salt of o-*toluidine* forms flat, brownish-red laths; the m-*isomeride*, glistening, red crystals, the p-*isomeride*, very small, lustrous, felted laths.

Of the isomeric *xylidine telluribromides*, the *o*-4-compound crystallises in lustrous, brownish-red platelets, the *m*-4-compound in small glistening plates, and the *p*-compound in small, brownish-red laths.

Pyridine telluribromide forms bright red laths or platelets, the 2-*methylpyridine* compound, small, lustrous needles, the quinoline salt, crystalline, red or orange-red granules, the *benzylamine* salt, large, lustrous, brownish-red leaflets, the *benzylethylamine* salt, small, bright red crystals, the α-*naphthylamine* salt, brownish-red platelets, and the β-*naphthylamine* salt, small, lustrous, orange-red leaflets.

The salts have been crystallographically examined by Lenk, who finds that the chloro-salts of aniline, methylaniline, diethyl-

aniline, *o*-toluidine, *o*-4-xylidine, pyridine, benzylethylamine, and the bromo-salts of propylenediamine, aniline, ethylaniline, diethylaniline, *p*-toluidine, benzylethylamine, and α-naphthylamine are rhombic, whilst the tellurichlorides of *m*- and *p*-toluidine, *p*-xylidine, quinoline, and α-naphthylamine, together with the bromo-salts of methylaniline, *o*- and *m*-toluidines, and the three xylidines crystallise in the monoclinic system. The telluribromides of *m*-4-xylidine and pyridine, and the chloro-salt of benzylamine are either rhombic or monoclinic. F. B.

o-**Nitrodialkylanilines.** GEORG WEISSENBERGER (*Monatsh.*, 1912, **33**, 821—841).—*o*-Chloronitrobenzene and dimethylamine in absolute alcoholic solution readily interact in presence of copper powder, giving nearly the theoretical quantity of *o*-nitrodimethylaniline. This and its homologues are yellow, oily liquids of strong odour, volatile in steam.

The influence of the nitro-group on the amino-group is evident in their behaviour towards nitrous acid, when no nitroso-compound is formed. They do not react with aldehydes or diazo-compounds. The ferrocyanides are soluble and not characteristic; the ferricyanides are insoluble. They are decomposed on heating, but can be distilled in a vacuum.

The hydrochlorides of the nitrodialkylanilines undergo a true thermal dissociation when heated into acid and base, the change taking place suddenly and at a definite temperature. It is shown not to be a case of primary melting and secondary dissociation.

Ammonia behaves somewhat differently towards copper powder than do its alkyl derivatives. When heated with *o*-chloronitrobenzene, the yield of *o*-nitroaniline is only about 1·5%.

The following salts of *o*-nitrodimethylaniline are described: the *sulphate* forms colourless platelets, which become yellow on exposure to the air, m. p. 126—127°; the *hydrobromide* forms short, colourless needles or rhombic prisms, decomp. 172°; the *hydriodide* dissociates at 126°; the *aurichloride* forms long, yellow prisms, which explode when heated in the air, but decompose and blacken at 152° in sealed tubes; the *ferrocyanide* forms short, brown prisms; the *ferricyanide* gives well-formed yellow crystals.

o-*Nitrodiethylaniline* is an orange-yellow oil of characteristic odour. The *picrate* forms lustrous, golden platelets, m. p. 119—120°; the *platinichloride* forms yellow, microscopic needles; the *aurichloride* gives pale yellow needles; the *sulphate* crystallises in broad tablets, m. p. 143°; the *hydrochloride* gives lustrous needles or short columns, decomp. 156°; the *hydrobromide* forms glass-like platelets, which are hygroscopic, decomp. 160°; the *hydriodide* forms colourless needles, which dissociate at 112°. The *ferrocyanide* crystallises in brown prisms; the *ferricyanide* forms long, yellow, monoclinic pyramids, which have sharp angles.

o-*Aminodiethylaniline* [*Diethyl*-o-*phenylenediamine*], prepared by reduction of the nitro-derivative with tin and hydrochloric acid, is a viscid, colourless oil of refreshing odour, b. p. 312·5°/744 mm. The *stannichloride* crystallises in bunches of silky needles, m. p. 145°; the

picrate gives golden-yellow prisms, m. p. 236°; the *hydrochloride* consists of long, colourless needles; the *aurichloride* forms pale yellow, short columns; the *platinichloride* separates in egg-yellow, microscopic needles; the sulphate forms long, colourless needles.

o-*Nitrodipropylaniline* yields a *picrate* crystallising in lustrous, golden needles, a yellow, crystalline *platinichloride*, an *aurichloride* consisting of microscopic, yellow prisms, and a *sulphate* forming colourless, feathery crystals. The *hydrochloride* is a crystalline powder; the *hydrobromide* forms lustrous platelets, and the *hydriodide* separates in short, colourless needles. The *ferricyanide* forms characteristic yellow crystals.

The following salts of *o*-nitroaniline are described: the *picrate* forms red, coral-like crystals, m. p. 73°; the *sulphate* gives colourless needles m. p. 144°; the *hydriodide* is characterised by lustrous platelets, which dissociate at 141°. E. F. A.

Action of Dilute Sulphuric Acid on Phenyl- and *p*-Tolylhydroxylamine, in the Presence and the Absence of Phenol. Eugen Bamberger (*Annalen*, 1912, **390**, 131—190).—Many of the results recorded in the paper have appeared in brief notices during the last twelve years. In short, the author's explanation of the transformation of arylhydroxylamines into *p*-aminophenols is represented by the scheme: $NHPh\cdot OH \longrightarrow C_6H_5\cdot N< + H_2O \longrightarrow {}^{H}_{OH}{>}C_6H_4{:}NH \longrightarrow OH\cdot C_6H_4\cdot NH_2$, the formation of by-products being explained by the addition of molecules other than those of water to the complex $C_6H_5\cdot N<$. When β-phenylhydroxylamine and dilute sulphuric acid (1 : 10 by vol.) are heated on a boiling-water bath, the main products are about equal quantities of *p*-aminophenol and azoxybenzene; in addition, about 10% of aniline, and small quantities of *p*-hydroxydiphenylamine, *p*-aminophenolsulphonic acid, benzidine, and *p*-aminodiphenylamine are produced.

When β-phenylhydroxylamine mixed with about ten times its weight of sand is slowly stirred into concentrated sulphuric acid at −18°, and the mixture is kept at 0° for seventy hours, the chief product is *p*-aminophenolsulphonic acid (in two forms, quadratic plates and slender needles); *p*-aminophenol is also produced, together with very small quantities of quinol and *pp'*-diaminodiphenyl oxide (?).

The interaction of β-phenylhydroxylamine, phenol (5 mols.), and sulphuric acid (1 : 3 by vol.) for five minutes at the b. p. yields aniline, *p*-aminophenol, a small quantity of a substance, m. p. 179° (probably 4-*amino-2'-hydroxydiphenyl*), and, as the most characteristic product, 4-*amino-4'-hydroxydiphenyl*, $OH\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, m. p. 271·5°, glistening needles. This substance forms a *hydrochloride* and a *sulphate*, both of which are sparingly soluble, and yields by diazotisation a *diazonium chloride*, $C_{12}H_9ON_2Cl,2H_2O$, which crystallises in red needles with a blue shimmer, the colour changing to yellow when the salt is dehydrated over sulphuric acid in a vacuum. The same colour change is produced by absolute alcohol, and from the yellow alcoholic solution, dry ether precipitates the anhydrous diazonium chloride in yellow needles, which rapidly absorb moisture in the air and become

red. The diazonium chloride can be recrystallised from boiling water without appreciable decomposition by rapid manipulation; its orange-red aqueous solution turns citron-yellow in the presence of hydrochloric acid, and intensely red in the presence of hydroxyl ions, the substance being an extraordinarily sensitive reagent for the detection of the latter. The diazonium chloride is converted into 4 : 4′-dihydroxydiphenyl by prolonged boiling of its aqueous solution.

In an atmosphere of carbon dioxide, β-*p*-tolylhydroxylamine reacts with cold dilute sulphuric acid in fourteen hours to form toluquinol, 4-iminotoluquinol being an intermediate product.

[With L. Blangey.]—By treatment for fourteen days at the ordinary temperature and then for the same time at 0°, toluquinol and methyl alcohol containing a little concentrated sulphuric acid yield toluquinol methyl ether, cresorcinol dimethyl ether, and a *substance*, m. p. 125—125·5°, needles or prisms, which is probably a trihydroxyditolyl trimethyl ether, $OMe{\cdot}C_6H_3Me{\cdot}C_6H_2Me(OMe)_2$, since it is converted by boiling hydriodic acid, D 1·7, into a *substance*, m. p. 187·5—188·5°, which is soluble in alkalis and has the composition of a trihydroxyditolyl.

The action of ethyl alcohol and sulphuric acid on toluquinol is quite similar; cresorcinol diethyl ether, *trihydroxyditolyl triethyl ether*, $C_{20}H_{26}O_3$, m. p. 77—77·5°, and *toluquinol ethyl ether* (5-*ethoxy*-o-*cresol*), $OEt{\cdot}C_6H_3Me{\cdot}OH$, m. p. 55—55·5°, are formed.

When heated on the water-bath for forty minutes with dilute sulphuric acid (1 : 10 by vol.), β-*p*-tolylhydroxylamine yields toluquinol, *p*-toluidine, and small quantities of *p*-azoxytoluene and 5-amino-*o*-cresol.

[With Josef Brun.]—By slowly stirring β-*p*-tolylhydroxylamine into concentrated sulphuric acid at −20°, and keeping the mixture at 0° for eighteen hours, there are produced an amorphous, reddish-yellow *base*, C_7H_7N, m. p. 155—160°, and an amorphous, dark grey *base*, $4C_7H_7N,H_2O$, sintering at about 220°; the compositions of the two bases are given with reserve.

In dilute sulphuric acid, β-*p*-tolylhydroxylamine and *p*-nitrotoluene do not interact, since the products, azoxytoluene, *p*-toluidine, and toluquinol, are the same as those obtained from β-*p*-tolylhydroxylamine and dilute sulphuric acid alone. When a mixture of the two tolyl compounds, however, is stirred slowly into concentrated sulphuric acid at −3° to 4°, and the mixture is kept for two days, the reaction yields the sulphate of 2-nitro-4′-amino-5-methyldiphenylmethane.

When heated with dilute sulphuric acid for twenty minutes, β-*p*-tolylhydroxylamine and phenol (4 mols.) yield *p*-azoxytoluene, *p*-hydroxyphenyl-*p*-tolylamine, and toluquinol. C. S.

Beckmann Rearrangement of Hydroxamic Acids. Lauder William Jones (*Amer. Chem. J.*, 1912, **48**, 1—28).—An account of the transformation of certain hydroxamic acids has been given by Thiele and Pickard (Abstr., 1900, i, 29), in the course of which phenylacethydroxamic acid, m. p. 121°, was described. A phenylacethydroxamic acid has now been obtained of m. p. 145—145·5°, which is probably isomeric with Thiele and Pickard's compound. The *benzoyl* derivative

of the new acid, $CH_2Ph{\cdot}CO{\cdot}NH{\cdot}OBz$, m. p. 120·5—121·5°, forms colourless needles, and yields a crystalline *potassium* salt which undergoes explosive decomposition accompanied by a Beckmann rearrangement at the ordinary temperature with formation of benzylcarbimide and potassium benzoate:

$$CH_2Ph{\cdot}C(OK){:}N{\cdot}OBz = CH_2Ph{\cdot}N{:}C{:}O + C_6H_5{\cdot}CO_2K.$$

The corresponding *sodium* salt is more stable, but suffers a similar decomposition when heated. The *silver* salt explodes after being heated for a few minutes at 70°. The *acetyl* derivative of phenylacethydroxamic acid, $CH_2Ph{\cdot}CO{\cdot}NH{\cdot}OAc$, m. p. 148—149°, forms long, flat crystals; its *potassium* salt does not decompose at 25°, but explodes if heated for four or five minutes at 50°. The *propionyl*, n-*butyryl*, and iso*butyryl* esters of phenylacethydroxamic acid have m. p. 138—139°, 113—114°, and 111—112° respectively.

A discussion is given of the mechanism of the Beckmann rearrangement, and evidence is presented in support of the views advanced by Stieglitz (Abstr., 1897, i, 43; 1903, i, 235). It is shown, however, that in the transformations of the hydroxamic acids there are certain factors, due to the influence of stereoisomerism, which cannot be fully explained by Stieglitz' hypothesis. E. G.

Syntheses in the Fatty Aromatic Series. VI. Preparation of Fatty Aromatic Thiocarbimides by the Thiuramdisulphide Method. Julius von Braun and H. Deutsch (*Ber.*, 1912, **45**, 2188—2198. Compare von Braun, Abstr., 1902, i, 271). Fatty aromatic thiocarbimides may be readily prepared by successive treatment of thiuramdisulphides with sodium and iodine. The yields are generally good, and all operations can be carried out in cold solutions.

An alcoholic solution of phenylethylamine was treated with carbon disulphide, and to the dithiocarbamate so formed, an alcoholic solution of iodine was added, whereon the *thiuramdisulphide*,

$$S(CS{\cdot}NH{\cdot}CH_2{\cdot}CH_2Ph)_2,$$

separated. It had m. p. 83—84°, with simultaneous decomposition into the corresponding thiocarbimide, *s*-dialkylthiocarbamide, sulphur, and hydrogen sulphide. When acted on successively by sodium and iodine it yielded phenylethylthiocarbimide, $C_2H_4Ph{\cdot}NCS$, b. p. 141—144°/11 mm. The latter combines with ammonia to form phenylethylthiocarbamide, m. p. 137°, with aniline to form phenylphenylethylthiocarbamide, m. p. 111° (Michaelis, Schröber, and Linow, Abstr., 1893, i, 703, give 106°), with phenylethylamine to form diphenylethylthiocarbamide, m. p. 95° (Neubert gives 85°). It also combines with fatty amines, yielding, for example, *phenylethyldimethylthiocarbamide*, m. p. 112°.

Phenylpropylamine was readily prepared by the reduction of phenylpropionitrile by means of sodium and alcohol. Like phenylethylamine, it yields a *thiuramdisulphide*,

$$S(CS{\cdot}NH{\cdot}CH_2{\cdot}C_2H_2{\cdot}CH_2Ph)_2,$$

m. p. 62°, which is more readily decomposed than the lower homologue, and similarly yields *phenylpropylthiocarbimide*, b. p. 156—160°/12 mm. (slight decomp.). The following thiocarbamides were prepared from

it; *phenylpropylthiocarbamide*, m. p. 111°; *phenylphenylpropylthiocarbamide*, m. p. 77°; di-phenylpropylthiocarbamide, m. p. 100°.

From phenylbutylamine an oily *thiuramdisulphide* was obtained, which was converted into *phenylbutylthiocarbimide*, b. p. 166—174°/12 mm. (slight decomp.). The latter united with the corresponding amines to form *phenylphenylbutylthiocarbamide*, m. p. 95°; *diphenylbutylthiocarbamide*, m. p. 49°; *phenylbutylpiperidylthiocarbamide*, m. p. 65°.

It is noteworthy that, whereas benzyl- and phenyl-ethylthiocarbimides possess powerful odours, phenylpropylthiocarbimide smells but faintly, and phenylbutylthiocarbimide is practically odourless when pure.

Benzhydrylamine yielded a yellow, oily, readily decomposable *thiuramdisulphide*, from which *benzhydrylthiocarbimide*, $CHPh_2\cdot N\colon CS$, m. p. 58° was prepared in good yield, and which was perfectly stable at the ordinary temperatures. The following thiocarbamides were prepared: *phenylbenzhydrylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CHPh_2$, m. p. 181°; *dibenzhydrylthiocarbamide*, m. p. 211°; *benzhydryl*isoamyl*thiocarbamide*, m. p. 110°. Benzhydrylthiocarbimide was further combined with hydrazine to yield *benzhydrylthiosemicarbazide*, m. p. 144°, the *benzylidene* derivative of which had m. p. 184°.

The *thiuramdisulphide* derived from anisamine was oily and readily decomposed, whilst the corresponding *thiocarbimide* could not be distilled without considerable decomposition. A fraction of b. p. 170—175°/16 mm., was isolated, which analysis showed to be pure. From it were obtained *phenylanisylthiocarbamide* and *dianisylthiocarbamide*, m. p. 142°.

The above method of preparing thiocarbimides appears to be general. Failure was met with *p*-nitrobenzylamine, the *thiuramdisulphide* of which, when treated with sodium ethoxide and subsequently with iodine, yielded no trace of thiocarbimide. H. W.

The System Water–*cyclo*Hexanol. ROBERT DE FORCRAND (*Compt. rend.*, 1912, **155**, 118—121).—A determination of the solidification temperatures of mixtures of water and *cyclo*hexanol up to a mixture containing 10% water. The curve is given and shows a eutectic at 4·73% water. The first portion of the curve is practically a straight line showing a constant molecular depression. The second half of the curve shows a notable inflexion in the neighbourhood of 9% water, corresponding with a compound, $C_6H_{11}\cdot OH + \frac{1}{2}H_2O$.

W. G.

Catalytic Preparation, by the Wet Method, of Esters Resulting from Cyclanols and Organic Acids. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1912, **155**, 168—170).—Esters of fatty alcohols and organic acids are readily obtained by the catalytic action of aluminium sulphate, potassium hydrogen sulphate, or sulphuric acid on a boiling mixture of the alcohol and acid, the best results being furnished by sulphuric acid (compare Abstr., 1911, i, 600, 637; ii, 1080). When applied to the *cyclo*hexanols a difficulty arises in that they are converted on boiling with 4% sulphuric acid into *cyclo*hexenes. This continues to take place to some extent even

in the presence of organic acids. By modifying the temperature, however, good yields of the esters can be obtained from these alcohols.

By mixing together *cyclo*hexanol (1 mol.) and formic acid (2 mols.) at the ordinary temperature and adding 4% sulphuric acid, an immediate reaction occurs, *cyclo*hexyl formate being produced without the formation of any *cyclo*hexene. A similar result is obtained with the three methyl*cyclo*hexanols. With the higher homologues of formic acid, the best results are obtained by keeping the mixture at 100—110° for one hour, when a yield of 90% is obtained. W. G.

Oxidation of *p*-Thymol. Dehydrodi-*p*-thymol. HENRI COUSIN and HENRI HÉRISSEY (*Compt. rend.*, 1912, **155**, 215—217 *).—*p*-Thymol (compare Guillaumin, Abstr., 1910, i, 375), like its isomerides thymol and carvacrol, is oxidised by ferric chloride or by the oxydase of mushrooms, giving dehydrodi-*p*-thymol (compare Abstr., 1908, i, 84, 727, 783; 1910, i, 476). *p*-Thymol is dissolved in alcohol, diluted with a large quantity of water, mixed with a solution of ferric chloride, and left to remain for six days at 16—18°. A pale yellow, voluminous precipitate slowly forms, which on purification gives crystals of *dehydrodi*-p-*thymol*, $OH\cdot C_6H_2Pr^{\beta}Me\cdot C_6H_2Pr^{\beta}Me\cdot OH$, m. p. 96—97°. This can be similarly prepared by replacing the ferric chloride by a glycerol extract of *Russula delica*, and keeping a current of air passing through the liquid. It gives no coloration with ferric chloride, is soluble in alkalis, being reprecipitated by acids, and generally exhibits phenolic characteristics. Benzoyl chloride, in the presence of alkalis, converts it into its *dibenzoyl* derivative, m. p. 184—185°. W. G.

Nitration of Guaiacol. ALFONS KLEMENC (*Monatsh.*, 1912, **33**, 701—707. Compare this vol., i, 459).—6-Nitroguaiacol was obtained previously (*loc. cit.*) by boiling 5-nitroveratric acid with aniline. It is more easily prepared in quantity by nitration of guaiacol dissolved in ether with red fuming nitric acid. A mixture of 45% of 6-nitroguaiacol, 25% of 4-nitroguaiacol, and a varying proportion of 4 : 6-dinitroguaiacol is obtained. The preponderance of 6- over 4-nitroguaiacol is unusual.

No nitro-derivative of acetylguaiacol could be obtained under similar conditions, but on nitrating in acetic acid in fairly concentrated solution, 5-nitroguaiacyl acetate was obtained as the sole product. Acetylation of a phenolic group decreases the velocity of nitration very much more than etherification. The nature of the solvent has very little influence.

Previously, 4-nitroguaiacol had only been prepared by way of *p*-nitrosoguaiacol (Rupe, Abstr., 1898, i, 72).

Further nitration of either 4- or 6-nitroguaiacol yielded the same dinitroguaiacol, identical with that described by Herzig (Abstr., 1884, 464).

Acetyl-6-nitroguaiacol crystallises in colourless platelets, m. p. 40°.

E. F. A.

Fluorene Series. III. JULIUS SCHMIDT, FRIEDRICH RETZLAFF, and AUGUST HAID (*Annalen*, 1912, **390**, 210—234).—When heated

* and *J. Pharm. Chim.*, 1912, [vii], **6**, 147—153; *Bull. Soc. Chim.*, 1912, [iv], **11**, 853—857.

with concentrated sulphuric acid on the water-bath, fluorene yields a mixture of three disulphonic acids, called the α, β, and γ respectively, which are isolated in the form of the barium salts. *Fluorene-α-disulphonic acid*, the barium salt of which is the least soluble, proves to be the 2 : 7-disulphonic acid. When heated with potassium hydroxide and a little water at 320—325° for about twenty minutes, potassium fluorene-2 : 7-disulphonate is converted into 2 : 7 : 9 : 9-*tetrahydroxyfluorene*, $\begin{matrix} C_6H_3(OH) \\ | \\ C_6H_3(OH) \end{matrix}\!\!>C(OH)_2$, m. p. 278° (*tetrabenzoate*, m. p. 260°). The positions of the hydroxyl groups are deduced from the following properties. When heated with phosphorus pentachloride at 250°, the tetrahydroxyfluorene is converted into 9 : 9-*dichloro*-2 : 7-*fluorenequinone*, $CCl_2\!\!<\!\!\begin{matrix} C_6H_3O \\ | \\ C_6H_3O \end{matrix}$, m. p. 165°, yellow needles, which is insoluble in alkalis. When heated with phosphorus pentachloride in a sealed tube for eight hours at about 220°, the tetrahydroxyfluorene is converted into 2 : 7 : 9 : 9-tetrachlorofluorene, m. p. 215°, colourless needles, identical with the compound obtained by Schmidt and Wagner from 2 : 7-dinitrofluorenone.

2 : 7-Dinitrofluorenone, which is best prepared by boiling fluorenone and red nitric acid, D 1·525, for two hours, is reduced by tin and hydrochloric acid to 2 : 7-*diaminofluorenone hydrochloride*,

$$C_{13}H_{10}ON_2,2HCl,$$

which does not melt at 360° and forms a *phenylhydrazone*,

$$C_{19}H_{16}N_4,2HCl,$$

yellow leaflets, sintering above 250°. 2 : 7-*Diaminofluorenone*, m. p. about 290°, dark violet needles, forms a *picrate*, m. p. 230° (decomp.), *phenylhydrazone*, m. p. 230° (decomp.), red needles, *oxime*, m. p. 255°, p-*nitrophenylhydrazone*, m. p. 280°, crimson needles, and *tetra-acetyl* derivative, m. p. 222°, yellow needles. By diazotisation and subsequent heating with water, 2 : 7-diaminofluorenone is converted into 2 : 7-*dihydroxyfluorenone*, red needles.

When treated with concentrated sulphuric acid and red nitric acid, D 1·525, fluorenone is converted into 2 : 3 : 6 : 7-*tetranitrofluorenone*, m. p. 248° (decomp.), yellow, rhombic plates. This compound, which is also obtained by heating 2 : 6 : 7-trinitrofluorenone with concentrated nitric and sulphuric acids, crystallises from glacial acetic acid in large, amber crystals containing $C_2H_4O_2$, forms an *oxime*, decomp. 249°, yellow needles (*acetyl* derivative, $C_{15}H_7O_{10}N_5$, m. p. 223°), and *semicarbazone*, m. p. 271° (decomp.), and is reduced by tin and hydrochloric acid to the *hydrochloride* of tetra-aminofluorenyl alcohol, $C_{13}H_{14}ON_4,4HCl$; the free base is extremely unstable.

2 : 3 : 6 : 7-Tetranitrofluorenone does not react with phenylhydrazine or *p*-nitrophenylhydrazine ; 2 : 6 : 7-trinitrofluorenone readily forms a p-*nitrophenylhydrazone*, decomp. 170—185°. C. S.

Splitting of Aminoarylcarbinols by the Action of Bromine. Latham Clarke and Richard Harkness Patch (*J. Amer. Chem. Soc.*, 1912, **34**, 912—917).—Clarke and Esselen (Abstr., 1911, i, 725) have shown that when a solution of 2 : 5-dibromo-4-aminobenzhydrol in

chloroform is treated with bromine, it is decomposed with formation of 2 : 4 : 6-tribromoaniline and benzaldehyde. It has since been found that this is a general reaction for aminobenzhydrols. The work has now been extended to aminoarylcarbinols containing an aliphatic residue, and also to tertiary carbinols.

By the action of bromine on 4-dimethylaminophenylethylcarbinol, *p*-bromodimethylaniline hydrobromide and propaldehyde are produced. 4-Dimethylaminophenyl*iso*butylcarbinol similarly yields *p*-bromodimethylaniline hydrobromide and *iso*valeraldehyde.

4-Dimethylaminodiphenylmethylcarbinol was obtained by Fecht (Abstr., 1907, i, 927) as an oil. If prepared from benzanilide, dimethylaniline, and phosphoryl chloride, it can be obtained in transparent prisms, m. p. 67°. When treated with bromine, it yields *p*-bromodimethylaniline hydrobromide and acetophenone.

Dimethylaminotriphenylcarbinol is decomposed by bromine with formation of a fair yield of *p*-bromodimethylaniline, but only a small quantity of benzophenone; it is probable that most of the carbinol is converted by the bromine into fuchsonedimethylimonium bromide. Tetramethyldiaminotriphenylcarbinol and hexamethyltriaminotriphenylcarbinol were also treated with a chloroform solution of bromine; in each case a small amount of *p*-bromodimethylaniline was obtained, but no ketone could be isolated, most of the carbinol having been converted into fuchsone derivatives. E. G.

The Action of Perhydrol on Cholesterol in the Presence of Sulphuric Acid. STÉPHANE MINOVICI and EUGÈNE VLAHUTZA (*Bull. Soc. chim.*, 1912, [iv], 11, 747—754).—When an intimate mixture of 10 grams of cholesterol, 33 c.c. of perhydrol, and 67 c.c. of sulphuric acid (D 1·8) is warmed on a water-bath with constant agitation, a clotted mass is obtained, which can be purified by solution in alkali, reprecipitation by dilute hydrochloric acid, and subsequent evaporation of the ethereal solution in a vacuum.

The white, amorphous acidic substance, m. p. 112° (decomp.), $[\alpha]_D$ +17·39° (in ether), thus obtained has the composition $C_{26}H_{46}O_5$ (probable structure given in formula I), and its formation from cholesterol (formula II) is explained by successive addition of

$$\text{(I.)}\quad \begin{matrix} CO_2H\cdot CH_2 \\ OH\cdot CH_2 \end{matrix}\!>\!C_{16}H_{24}\!<\!\begin{matrix} CH_2\cdot CH_2\cdot CHMe_2 \\ CH(OH)\cdot CH_2\cdot OH \end{matrix}$$

$$\text{(II.)}\quad OH\cdot CH\!<\!\begin{matrix} CH_2 \\ CH_2 \end{matrix}\!>\!C_{17}H_{26}\!<\!\begin{matrix} CH_2\cdot CH_2\cdot CHMe_2 \\ CH{:}CH_2 \end{matrix}$$

hydroxyl groups at the vinyl group, oxidation of the cyclic alcoholic radicle to a ketonic group with subsequent disruption of the ring, and finally elimination of a methyl group from the $C_{17}H_{26}$ nucleus.

The *potassium*, *sodium*, *caesium*, and *rubidium* salts are deliquescent; the amorphous *ammonium* salt, m. p. 150° (decomp.), was obtained by the action of an alcoholic solution of ammonia on an ethereal solution of the acid. The *silver* salt, a red amorphous powder, on treatment with the calculated amount of methyl iodide yields the *methyl* ester, an amorphous powder, m. p. 70°. The other esters are generally of syrupy consistency. D. F. T.

The Formation of Basic Derivatives of Cholesterol and the Preparation of α-Cholestylamine. OTTO DIELS and ERICH STAMM (*Ber.*, 1912, 45, 2228—2232).—Cholesterol readily reacts with chloroacetyl chloride to form cholesteryl chloroacetate, from which cholesteryl piperidylacetate can be prepared. The corresponding amino-derivative could not be obtained by the action of ammonia. α-Cholestylamine was obtained by the reduction of α-cholestanoneoxime. The latter substance and the corresponding semicarbazone have unexpectedly low and indefinite m. p.'s, possibly owing to the formation of liquid crystals.

Cholesteryl chloroacetate, prepared by warming cholesterin with chloroacetyl chloride, has m. p. 162°. *Cholesteryl piperidylacetate* has m. p. 114·5°. The *hydrochloride* of the latter was analysed.

α-Cholestanone-p-*nitrophenylhydrazone* separates from alcohol in yellow needles, which soften at 179°, and are completely melted at 184°.

α-Cholestanoneoxime is a white, amorphous powder, which softens at 75°, and has m. p. 95—100°. It forms a well-crystallised additive *product* with carboxyethylcarbimide, m. p. 161° (decomp.). When reduced by sodium in boiling amyl-alcoholic solution, it is transformed into *α-cholestylamine*, m. p. 110—120°, the *hydrochloride* of which was also analysed. H. W.

Chlorination of Benzoic Acid. J. TH. BORNWATER and ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1912, 31, 221—248).—An endeavour to clear up the question as to the result of chlorinating benzoic acid (compare Claus and Bücher, Abstr., 1887, 828; Lossen, 1904, i, 159). In this paper the question is only dealt with from the qualitative side. In the first part of the paper directions are given for the preparation of the pure mono- and di-chlorobenzoic acids from various derivatives of toluene, after which some of the physical properties of the monochlorobenzoic acids are compared, from which a method for the qualitative separation of benzoic and the monochlorobenzoic acids is drawn up.

By the action of chlorine on a slight excess of benzoic acid in the presence of ferric chloride at about 20°, in the absence of light, the principal product is *m*-chlorobenzoic acid, together with some 2 : 5- and 3 : 4-dichlorobenzoic acids. When one atom of chlorine has been introduced, the rate of substitution is much greater, and the second entrant chlorine atom seems to be directed by the atom already present rather than by the carboxyl group.

On chlorinating benzoyl chloride by the passage of a current of chlorine with intermittent exposure to light, additive products are formed, the principal one being the hexachloride of benzoic acid, together with some benzene hexachloride.

The last part of the paper contains fusion-point curves and tables of results for mixtures of benzoic acid with each of the monochloro-acids, and also mixtures of the three monochloro-acids taken in pairs. W. G.

Derivatives of Ethyl α-Cyanophenylacetate and Ethyl α-Cyanobutyrate. HARRY F. HADLEY (*J. Amer. Chem. Soc.*, 1912, **34**, 923—928).—α-Cyanophenylacetic and α-cyanobutyric acids each contain an asymmetric carbon atom. The present work was undertaken with the object of separating the acids into their two enantiomorphic modifications. The salts of α-cyanophenylacetic acid proved too unstable for the purpose. Attempts were made to resolve α-cyanobutyric acid by means of its metallic salts and also by the fractional crystallisation of its salts with optically active alkaloids, but in each case without success.

Lead and *cadmium* α-cyanophenylacetates, and *barium*, *strontium*, *strychnine*, and *brucine* α-cyanobutyrates were prepared and analysed. *Aniline* α-cyanobutyrate, has m. p. 57°; the *anilide* was also prepared.

α-Cyano-α-ethylbutyranilide, m. p. 217—218°, crystallises in long needles; the corresponding p-*toluidide* was also prepared. E. G.

Influence of Calcium Benzoate on the Solubility of Calcium Cinnamate. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1912, **31**, 256—257).—A solution of calcinm benzoate saturated at 26°, on warming dissolves calcium cinnamate, and from the solution, on cooling, there separate out crystals of a double salt having the composition $CHPh:CH\cdot CO_2\cdot Ca\cdot CO_2Ph,3H_2O$. W. G.

Derivatives of Diphenylbromoacetic Acid. HEINRICH KLINGER and G. NICKELL (*Annalen*, 1912, **390**, 365—370).—*Diphenylbromoacetyl bromide*, $CPh_2Br\cdot COBr$, m. p. 64—65°, obtained by heating benzilic acid and phosphorus pentabromide (2 mols.) on the water-bath, is converted by warm aniline into *diphenylanilinoacetanilide*, m. p. 181—182°, and by ethereal aniline (2 mols.) into *diphenylbromoacetanilide*, m. p. 85—86°.

When diphenylchloro- or bromo-acetanilide is heated at 140—230° for one and a-half hours, each yields a *substance* which crystallises from benzene in prismatic needles containing C_6H_6, m. p. 225—226°, and may possibly be 1 : 3 : 3 : 4 : 6 : 6-*hexaphenyl*-2 : 5-*diketopiperazine*.

Diphenylaminoacetamide, $NH_2\cdot CPh_2\cdot CO\cdot NH_2$, m. p. 144—145°, is obtained by passing dry ammonia into a cold ethereal solution of diphenylbromoacetyl bromide. C. S.

The Condensation of Phenylglycollonitrile with Aromatic Aldehydes in the Presence of Thionyl Chloride. STÉPHANE MINOVICI and Mlle. THÉODOSIE ZENOVICI (*Bull. Soc. chim.*, 1912, [iv], **11**, 757—762).—Aromatic aldehydes can condense in several ways with phenylglycollonitrile (E. Fischer, Abstr., 1896, i, 262; Minovici, Abstr., 1899, i, 890; *Bull. de Chim. Roum.*, 1910, No. 1). The final product of the action of thionyl chloride on a mixture of an aromatic aldehyde with phenylglycollonitrile is of the structure $(CHPhCl\cdot CO\cdot NH)_2R$, where R represents the benzylidene or some analogous radicle; chlorophenylacetonitrile, $CHPhCl\cdot CN$, and chlorophenylacetamide, $CHPhCl\cdot CONH_2$, are probably intermediate products.

Thionyl chloride is cautiously added to an equimolecular quantity

of phenylglycollonitrile, and after thirty-six hours, an equimolecular quantity of aromatic aldehyde is introduced. After a time the mass solidifies; after extracting with ether, the residue is recrystallised from alcohol.

Benzylidenebisphenylchloroacetamide, $(CHPhCl\cdot CO\cdot NH)_2CHPh$, obtained in the above manner using benzaldehyde, forms plates or fine needles, m. p. 192—194°.

p-*Methoxybenzylidenebisphenylchloroacetamide*,

$$(CHPhCl\cdot CO\cdot NH)_2CH\cdot C_6H_4\cdot OMe,$$

prepared with the use of anisaldehyde, forms silky needles, m. p. 196—198°.

p-iso*Propylbenzylidenebisphenylchloroacetamide*,

$$(CHPhCl\cdot CO\cdot NH)_2CH\cdot C_6H_4\cdot CHMe_2,$$

obtained analogously from cuminaldehyde, forms needles, m. p. 197—199°.

These three substances are hydrolysed by dilute hydrochloric acid in a sealed tube at 120°, giving the corresponding aldehyde together with phenylglycollic acid and ammonium chloride. They also react with aniline or phenylhydrazine on gentle warming; the action of aniline gives *benzylidenebisphenylanilinoacetamide*,

$$(NHPh\cdot CHPh\cdot CO\cdot NH)_2CHPh,$$

m. p. 202°; p-*methoxybenzylidenebisphenylanilinoacetamide*,

$$(NHPh\cdot CHPh\cdot CO\cdot NH)_2CH\cdot C_6H_4\cdot OMe,$$

m. p. 193°, and p-iso*propylbenzylidenebisphenylanilinoacetamide*,

$$(NHPh\cdot CHPh\cdot CO\cdot NH)_2CH\cdot C_6H_4\cdot CHMe_2,$$

m. p. 220°, all crystallising in needles. The action of phenylhydrazine gives three analogous substances, likewise crystallising in needles; *benzylidenebisphenylphenylhydrazinoacetamide*,

$$(NHPh\cdot NH\cdot CHPh\cdot CO\cdot NH)_2CHPh,$$

m. p. 183° (decomp.); p-*methoxybenzylidenebisphenylphenylhydrazinoacetamide*, $(NHPh\cdot NH\cdot CHPh\cdot CO\cdot NH)_2CH\cdot C_6H_4\cdot OMe$, m. p. 187° (decomp.), and p-iso*propylbenzylidenebisphenylphenylhydrazinoacetamide*, $(NHPh\cdot NH\cdot CHPh\cdot CO\cdot NH)_2CH\cdot C_6H_4\cdot CHMe_2$, m. p. 196° (decomp.). D. F. T.

The Saponification of a Cyanohydrazone. C. GASTALDI (*Gazzetta*, 1912, **42**, i, 612—617).—The hydrolysis of *a*-nitrophenylacetonitrile yields, instead of a carboxylic acid, *ω*-nitrophenylmethane, carbon dioxide being lost (Wislicenus and Endres, Abstr., 1902, i, 541). The hydrolysis of the similarly constituted phenylcyanoformaldehyde-*o*-nitrophenylhydrazone, $CN\cdot CPh\colon N\cdot NH\cdot C_6H_4\cdot NO_2$, has therefore been studied, and it is found that saponification proceeds in the usual manner, but that carbon dioxide may be eliminated by heating the product to fusion.

Phenylglyoxylic acid o-*nitrophenylhydrazone*,

$$CO_2H\cdot CPh\colon N\cdot NH\cdot C_6H_4\cdot NO_2,$$

prepared by heating the cyano-compound with 10% alcoholic potash, separates from benzene in yellow crystals, m. p. 180—181°. The *potassium* salt forms rose-coloured crystals, with $2H_2O$; the *silver* salt forms a pink, crystalline powder. The acid yields benzaldehyde-*o*-nitrophenylhydrazone on fusion. C. H. D.

Derivatives of Alkyloxydiphenylacetic Acid and Alkyloxydiphenyleneacetic Acid. HEINRICH KLINGER (*Annalen*, 1912, **390**, 371—376).—The halogen atoms in diphenylchloro- and bromo-acetic acids are much more easily displaced than those in diphenylene chloro- and bromo-acetic acids. Thus diphenylbromoacetyl bromide in methyl alcohol at 0° yields a substance, b. p. 191—192°/19 mm., which is converted by hydrolysis into *diphenylmethoxyacetic acid*,

$$OMe{\cdot}CPh_2{\cdot}CO_2H,$$

m. p. 99—100°.

Diphenylethoxyacetic acid, m. p. 113—114°, is obtained in a similar manner from diphenylbromoacetyl bromide and ethyl alcohol. Diphenylchloroacetyl chloride and alcohol yield 65% of ethyl diphenylchloroacetate.

Methyl diphenylenemethoxyacetate, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}{>}C(OMe){\cdot}CO_2Me$, m. p. 124°, and the *ethyl* ester, m. p. 72°, are obtained by heating the corresponding esters of diphenylenechloroacetic acid with methyl-alcoholic silver nitrate. By hydrolysis they yield *diphenylenemethoxyacetic acid*, m. p. 181° (decomp.). Diphenylenebromoacetanilide and methyl-alcoholic silver nitrate yield *diphenylenemethoxyacetanilide*,

$$\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}{>}C(OMe){\cdot}CO{\cdot}NHPh,$$

m. p. 195—196°.

Diphenylene-ethoxyacetic acid, m. p. 169°, is obtained by the hydrolysis of its *methyl* ester, m. p. 77°. *Diphenylene-ethoxyacetanilide*, m. p. 129—130°, is prepared from alcoholic silver nitrate and diphenylene-chloro- or -bromo-acetanilide. C. S.

Behaviour of Acid Dichlorides towards Ammonia. JOHANNES SCHEIBER and MAX KNOTHE (*Ber.*, 1912, **45**, 2252—2259).—The authors have examined the absorption spectra and the action towards ammonia of a number of acid dichlorides, and draw the conclusion that the formation of a nitrile acid by the interaction of an acid dichloride and ammonia cannot be regarded as evidence of the unsymmetrical structure of the former, but only shows a spatial proximity of the $-COCl$ groups, or of the $-COCl$ and $-SO_2Cl$ groups.

cis- and *cis-trans*-Camphoryl chlorides in ethereal solution have absorption spectra which are similar and appreciably stronger than that of *cis*-camphoric acid (measured in aqueous solution in the form of its sodium salt).

Quinolinyl dichloride, b. p. 159°/19 mm., was prepared by the action of phosphorus pentachloride on quinolinic acid. Its symmetrical nature was shown by the formation of the same dimethyl ester from quinolinyl dichloride and sodium methoxide as from silver quinolinate and methyl iodide, whilst, also, the absorption spectra of quinolinic acid (in alcohol), methyl quinolinate (in ether), and quinolinyl dichloride (in ether) were similar. Aqueous ammonia transformed quinolinyl dichloride into 3-*cyanopyridine*-4-*carboxylic acid*, m. p. 175—176°, the constitution of which follows from its hydrolysis to nicotinic acid.

*iso*Phthalyl and terephthalyl dichlorides were quantitatively transformed by ammonia into the corresponding diamides.

Comparison of the absorption curves of *o*-toluenesulphonic acid and its chloride showed that the transformation of the group $-SO_2 \cdot OH$ into $-SO_2Cl$ did not alter the nature of the absorption, which is increased. *o*-Sulphobenzoyl dichloride (m. p. 40°) was found to show an absorption similar to that of *o*-sulphobenzoic acid, whilst the isomeric chloride (m. p. 79°) showed much weaker absorption. Contrary to the usual practice, the authors consider the dichloride (m. p. 40°) to be symmetrical; that of m. p. 79° to be unsymmetrical. H. W.

[Solutions of Hydrogen Cyanide and Benzaldehyde.] P. WIRTH (*Arch. Pharm.*, 1912, **250**, 396—397).—The author replies to Rosenthaler's criticisms (Abstr., 1911, i, 987) of his work (Abstr., 1911, i, 875). C. S.

***o*- and *p*-Mercaptobenzaldehyde.** PAUL FRIEDLÄNDER and EMIL LENK (*Ber.*, 1912, **45**, 2083—2090).—Starting from *o*- and *p*-aminobenzaldehydes, *o*- and *p*-aldehydophenyl mercaptans, the first aldehydomercaptans to be prepared, have been obtained as volatile oils which easily polymerise.

o-Nitrobenzyl chloride when warmed with a solution of sulphanilic acid and excess of sodium carbonate, then treated with a solution of common salt and with a solution of sulphur in aqueous sodium hydroxide, and finally distilled with steam gives *o*-aminobenzaldehyde; this can be diazotised by dissolving in alcohol with the calculated quantity of nitrite and adding gradually to cold dilute sulphuric acid.

[*p*-Diazobenzaldehyde couples with β-naphthol giving p-*aldehydobenzeneazo-β-naphthol*, needles, m. p. 183°, which reacts easily with hydrazine, phenylhydrazine, and hydroxylamine. *m*-Diazobenzaldehyde in a similar manner gives m-*aldehydobenzeneazo-β-naphthol*, orange-red needles, m. p. 156°. *o*-Diazobenzaldehyde likewise couples with β-naphthol, giving a red dye, but this rapidly isomerises to 3-hydroxy-indazolyl-2-β-naphthol, $C_6H_4{<}\underset{C(OH)}{\overset{N}{|}}{>}N \cdot C_{10}H_6 \cdot OH$, a colourless substance, m. p. 235° (compare Bamberger and Lublin, Abstr., 1909, i, 509); the coupling product with α-naphthol is similarly rearranged to 3-*hydroxyindazolyl*-2-α-*naphthol*, colourless needles, m. p. 238°.]

If a diazotised solution of *o*-aminobenzaldehyde sulphate is run into a suspension of cuprous thiocyanate in a solution of potassium thiocyanate, o-*thiocyanobenzaldehyde*, $CHO \cdot C_6H_4 \cdot SCN$, colourless needles, m. p. 76°, is obtained; on mixing this with a warm aqueous solution of sodium sulphide and cooling, the *sodium* salt of o-*mercaptobenzaldehyde* separates in yellow crystals; free o-*mercaptobenzaldehyde* (o-*aldehydophenyl mercaptan*), $SH \cdot C_6H_4 \cdot CHO$, liberated by cautious treatment with acids, is a yellow oil of mercaptan-like odour, which on keeping quickly changes to a yellow resin. Oxidation of the mercaptan compound with potassium ferricyanide gives *dibenzaldehyde* o-*disulphide*, $S_2(C_6H_4 \cdot CHO)_2$, yellow needles, m. p. 145°. Other derivatives of the mercaptobenzaldehyde are o-*methylthiolbenzaldehyde*, $SMe \cdot C_6H_4 \cdot CHO$ (obtained by the action of methyl sulphate), which gives an *azine*, $SMe \cdot C_6H_4 \cdot CH{:}N \cdot N{:}CH \cdot C_6H_4 \cdot SMe$, yellow leaflets,

m. p. 119°, *phenylhydrazone*, m. p. 127—129°, and *thionaphthen*-2-*carboxylic acid*, $C_6H_4<\substack{CH \\ S}>C\cdot CO_2H$ (obtained by the action of sodium chloroacetate), colourless needles, m. p. 114°. The last-named derivative on heating with quicklime gives thionaphthen.

p-Aminobenzaldehyde can be obtained by the action on *p*-nitrotoluene of a solution of sulphur in aqueous sodium hydroxide; it is then diazotised and run into a solution of cuprous and potassium thiocyanates, when p-*thiocyanobenzaldehyde* is obtained, almost colourless needles, m. p. 78°; this substance reacts with an aqueous solution of sodium sulphide, giving the sodium salt of p-*mercaptobenzaldehyde*. This sodium salt can also be obtained by running the diazotised solution of *p*-aminobenzaldehyde into a solution of excess of potassium xanthate and subsequently hydrolysing the resultant *ethyl* p-*aldehydophenyl xanthate*, $CHO\cdot C_6H_4\cdot S\cdot CS\cdot OEt$ (m. p. 135°), with sodium hydroxide. p-*Mercaptobenzaldehyde* is a colourless oil (*sodium* salt, yellow leaflets), which quickly polymerises to a white solid, m. p. about 130°; this on treatment with sodium hydroxide solution gives the salt of the simple substance. The unimolecular compound gives a *phenylhydrazone*, m. p. 137°, and can be oxidised by potassium ferricyanide to the *disulphide*, yellow needles, m. p. 108°; the last substance gives a *phenylhydrazone*, leaflets, m. p. 198°. p-*Methylthiolbenzaldehyde*, a colourless oil, b. p. 273° (obtained by the action of methyl sulphate on the mercaptan), gives an *oxime*, m. p. 110°, a *phenylhydrazone*, leaflets, m. p. 138°, and an *azine*, yellow needles, m. p. 119°. D. F. T.

The Partial Catalytic Hydrogenation of Substances Containing more than One Double Bond. CARL PAAL (*Ber.*, 1912, **45**, 2221—2228. Compare Paal and Hartmann, Abstr., 1909, i, 926).—The author has studied the partial reduction of styryl methyl ketone, cinnamylidenemalonic acid, piperic acid, piperine, phorone, and distyryl ketone, and draws the conclusion that only those compounds possessing two double bonds in which the latter are separated by at least one carbon atom are capable of partial reduction. In all experiments, colloidal palladium was used as catalyst.

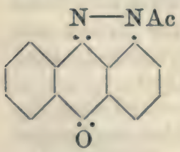
An alcoholic solution of styryl methyl ketone, when treated with the amount of hydrogen necessary for half-reduction, yielded unchanged styryl methyl ketone and δ-phenylbutyl methyl ketone. Similarly, the half-reduction of an aqueous solution of sodium cinnamylidenemalonate led to the isolation of unchanged cinnamylidenemalonic acid and ω-phenyl-*n*-propylmalonic acid. Piperic acid yielded *tetrahydropiperic acid*, m. p. 90—91°, together with unchanged piperic acid, whilst tetrahydropiperine and unchanged piperine were obtained when the latter was reduced.

Phorone, on the other hand, absorbed hydrogen very readily with the practically quantitative formation of *dihydrophorone* (*iso*butyl *iso*butenyl ketone), b. p. 176°. Its *semicarbazone* had m. p. 133—134°. Similarly, the main product of the half-reduction of distyryl ketone was phenylethyl styryl ketone. Dibenzylacetone was also formed in small quantity, together with substances of higher and less constant m. p.

When the solutions of phenylethyl styryl ketone were exposed to light, two *substances*, m. p. 125—126° and 180—188° respectively, were formed. H. W.

Anthraquinonylmonohydrazines. RICHARD MÖHLAU [with ARTUR VIERTEL and FR. REINER] (*Ber.*, 1912, **45**, 2233—2244).—The preparation and properties of anthraquinonyl-1-hydrazine and anthraquinonyl-2-hydrazine are described.

Anthraquinonyl-1-*diazonium hydrogen sulphate* was prepared by the addition of sodium nitrite to a suspension of 1-aminoanthraquinone sulphate. When acted on by potassium hydroxide and potassium sulphite, it was transformed into *potassium anthraquinonyl*-1-*diazosulphonate*, $C_{14}H_7O_5N_2SK$, whilst, under the action of potassium sulphite and a little potassium hydroxide followed by heating the solution to 90°, *potassium anthraquinonyl*-1-*hydrazinedisulphonate*, $C_{14}H_7O_2\cdot N(SO_3K)\cdot NH\cdot SO_3K,2H_2O$, was formed. *Anthraquinonyl*-1-*hydrazine*, m. p. 210° (corr., decomp.), was prepared by reduction of the diazosulphonate by stannous chloride and hydrochloric acid. Its *hydrochloride* was analysed. By the action of equimolecular quantities of potassium anthraquinonyl-1-hydrazine disulphonate and the corresponding aldehyde in alcoholic solution in the presence of concentrated hydrochloric acid, the following hydrazones were prepared, the colours of which are appended: *benzylideneanthraquinonyl*-1-*hydrazone* (dark brownish-red), m. p. 214°, and its *acetyl* derivative (light yellow), m. p. 234°; o-*nitrobenzylideneanthraquinonyl*-1-*hydrazone* (reddish-brown), m. p. 268—270°; m-*nitrobenzylideneanthraquinonyl*-1-*hydrazone* (brownish-red), m. p. 285—287°; p-*nitrobenzylideneanthraquinonyl*-1-*hydrazone* (red), m. p. above 300°; *dimethyl*-p-*aminobenzylideneanthraquinonyl*-1-*hydrazone* (dark blue), m. p. 234—235°; o-*hydroxybenzylideneanthraquinonyl*-1-*hydrazone* (dark violet), m. p. 258—260°; p-*hydroxybenzylideneanthraquinonyl*-1-*hydrazone* (dark violet), m. p. 275—276°; p-*methoxybenzylideneanthraquinonyl*-1-*hydrazone* (deep violet with bronze glance), m. p. 232°; *piperonylanthraquinonyl*-1-*hydrazone* (deep violet), m. p. 253°; *cinnamylideneanthraquinonyl*-1-*hydrazone* (brownish-red), m. p. 201—202°; *ethyl anthraquinonyl*-1-*hydrazoneacetoacetate* (reddish-brown), m. p. 169·5°. The latter substance, when treated with acetic anhydride and concentrated sulphuric acid, was transformed into *acetylpyrazoleanthrone* (annexed formula), m. p. 213° (corr.), which, under the action of alcoholic potassium hydroxide, followed by acidification, yielded *pyrazoleanthrone*, m. p. 277—278°. This substance was also obtained by heating anthraquinonyl-1-hydrazine with aniline and aniline hydrochloride at 150°.



Anthraquinonyl-2-*diazonium hydrogen sulphate* was prepared in the same manner as its isomeride (see above). It united with phenylmethylpyrazolone in aqueous solution in the presence of sodium acetate with the formation of 2-*anthraquinonyl*-4-*diazo*-1-*phenyl*-3-*methyl*-5-*pyrazolone*, which was obtained in yellow needles and red leaflets. Each form has m. p. 247° and shows the same absorption

spectrum. At temperatures above 110°, the yellow modification is readily transformed into the red variety. *Potassium anthraquinonyl-2-hydrazinedisulphonate* was obtained by the same method as the 1-compound. When boiled with concentrated hydrochloric acid, it yielded the *hydrochloride* of *anthraquinonyl-2-hydrazine*, whilst, when boiled with 40% alcohol, it formed *potassium anthraquinonyl-2-hydrazinesulphonate.*

Anthraquinonyl-2-hydrazine, m. p. 229°, was prepared by boiling potassium anthraquinonyl-2-hydrazinedisulphonate with hydrochloric acid and subsequent treatment with sodium acetate. Its *hydrochloride* has m. p. 238—239° (decomp.). The following hydrazones were prepared by the action of the hydrazine with the requisite aldehyde or ketone in alcoholic or pyridine solution: *benzylideneanthraquinonyl-2-hydrazone* (dark red), m. p. 286°; p-*nitrobenzylideneanthraquinonyl-2-hydrazone* (yellowish-red), m. p. above 330°; *dimethyl*-p-*aminobenzylideneanthraquinonyl-2-hydrazone* (dark violet), m. p. about 280°; o-*hydroxybenzylideneanthraquinonyl-2-hydrazone* (dark red), m. p. 334°; p-*hydroxybenzylideneanthraquinonyl-2-hydrazone* (dark violet), m. p. above 295°; p-*methoxybenzylideneanthraquinonyl-2-hydrazone* (reddish-violet), m. p. 280—284°; *piperonylanthraquinonyl-2-hydrazone* (brownish-red), m. p. about 290°; 2:3-*dihydroxybenzylideneanthraquinonyl-2-hydrazone* (deep blue), m. p. about 310°; p-*hydroxy*-m-*methoxybenzylideneanthraquinonyl-2-hydrazone* (yellowish-red), m. p. 307—308°; *cinnamylideneanthraquinonyl-2-hydrazone* (reddish-brown), m. p. 259°; *acetoneanthraquinonyl-2-hydrazone* (red), m. p. 228°; *benzophenoneanthraquinonyl-2-hydrazone* (brownish-red), m. p. 227°; *dibenzylideneanthraquinonyl-2-hydrazone* (reddish-orange), m.p. 273°; the *anthraquinonyl-2-hydrazone* of *ethyl acetoacetate* (yellowish-orange), m. p. 178°. The latter compound, unlike the corresponding 1-isomeride, can be converted into a pyrazolone. Under the action of boiling acetic anhydride, it was transformed into 1-β-*anthraquinonyl-5-acetyl-3-methylpyrazolone*, m. p. 237°, after darkening at 225°. H. W.

A New Synthesis of Anthraquinonylhydrazines. RICHARD MÖHLAU [with ARTUR VIERTEL and ALFRED REDLICH] (*Ber.*, 1912, **45**, 2244—2248).—Anthraquinonylhydrazines may be prepared by the interaction of hydrazine and α-chloroanthraquinones.

Anthraquinonyl-1-hydrazine was prepared by boiling a solution of 1-chloroanthraquinone in pyridine with hydrazine hydrate during thirty minutes. In similar circumstances, 2-chloroanthraquinone and hydrazine hydrate do not react, but, when heated during eight hours at 170°, anthraquinonyl-2-hydrazine is formed. Similarly, 5-*chloroanthraquinonyl-1-hydrazine*, m. p. 227°, was formed when 1:5-dichloroanthraquinone and hydrazine hydrate were boiled in pyridine solution. When the above substance, or more simply 1:5-dichloroanthraquinone itself, was heated with hydrazine hydrate and pyridine at 145° during eight hours, *anthraquinonylene-1:5-dihydrazine*, m. p. 258°, was formed, which was converted by acetic anhydride into an *acetyl* compound. When a solution of the dihydrazine in concentrated sulphuric acid was warmed, a *dipyrazoleanthrone* was formed. 1:8-Dichloroanthraquinone, when boiled with hydrazine

hydrate in pyridine solution, formed transitorily 8-*chloroanthraquinonyl-1-hydrazine*, which passed into 8-*chloropyrazoleanthrone*, m. p. above 360°.

2 : 6-Dichloroanthraquinone was converted in small yield into *anthraquinonylene*-2 : 6-*dihydrazine*, m. p. above 360°, when heated with hydrazine hydrate and pyridine during eight hours at 170°

H. W.

Artificial Caoutchouc. CARL D. HARRIES (*Zeitsch. angew. Chem.*, 1912, 25, 1457—1462). **Synthetic Caoutchouc** FRITZ HOFFMANN (*ibid.*, 1462—1467).—Lectures delivered before the Vereins Deutscher Chemiker at Freiburg in Breisgau dealing with the subject respectively from the scientific and the technical point of view.

Chemistry of Caoutchouc. V. Theory of Vulcanisation. III. DAVID SPENCE and J. YOUNG (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 28—34. Compare Abstr., 1911, i, 657).—Further experiments relating to the nature of the vulcanisation process have been made, in which the velocity of the change was determined. Pure white Ceylon-Para caoutchouc was intimately mixed with 10% of precipitated sulphur, and the vulcanisation carried out at a constant temperature (135° or 155°). After measured time intervals, the "fixed" sulphur was estimated, and the data thus obtained show that the reaction takes place at a constant speed. From the observed velocities at the two temperatures, the temperature-coefficient of the reaction is found to be 2·65. When the vulcanisation was carried out with 37% of sulphur, a similar constant velocity was observed, but instead of the whole of the sulphur being fixed, it was found that the process is completed when the proportion of fixed sulphur reaches 32%. This corresponds very closely with that required by the formula $C_{10}H_{16}S_2$, and this fact, together with the velocity observations, are considered to prove the untenability of the adsorption theory. The vulcanisation process, according to the authors, must therefore be considered essentially as a chemical process in which the above compound is formed.

Experiments on the vulcanisation of balata under the same conditions show that the course of the process is not only similar to that of the vulcanisation of caoutchouc, but that the velocity is very nearly the same in the two cases. H. M. D.

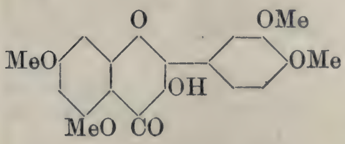
[Chemistry of Caoutchouc. Theory of Vulcanisation.] WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 34—36).—Polemical against Spence (compare previous abstract).

H. M. D.

The Desulphurisation of Vulcanised Caoutchouc. F. WILLY HINRICHSEN and ERICH KINDSCHER (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 38—39).—The values obtained for the combined sulphur by treatment of vulcanised caoutchouc with metals in presence of alcoholic sodium hydroxide solution (compare *ibid.*, 1912, 10, 146) cannot be accepted as correct, in that this method fails to take into

account the sulphur which may be combined with inorganic constituents. It is now shown that a correction for this may be applied by estimation of the sulphur in the ash. When this correction is applied to the sulphur content of the extracted material, it is found that the observed percentage of combined sulphur diminishes considerably as the pressure in the autoclave, in which the disulphurisation is effected, is increased from four to ten atmospheres. The acetone soluble constituents are also found to vary to a very large extent according to the pressure. H. M. D.

Methylation of Glucosides. JOSEF HERZIG and R. SCHÖNBACH (*Monatsh.*, 1912, 33, 673—681).—On methylation of quercitrin with diazomethane, the free hydroxyl groups in the quercetin residue are readily methylated, whilst one methy group is slowly introduced into the rhamnose residue, a pentamethylquercitrin being obtained.



This when decomposed with dilute acids yields a colourless tetramethylquercetin, which probably has the annexed constitution (see following abstract).

The nature of the attachment of quercetin to rhamnose is thus established.

The monomethyl rhamnose has been obtained only as a syrup, yielding amorphous derivatives. Pentamethylquercitrin could not be hydrolysed by enzymes.

On methylation of strophantin a halt is reached at a compound, $C_{43}H_{72}O_{19}$, containing four methoxyl groups. On acid hydrolysis, strophantidin and a tetramethoxystrophantobiose are obtained; the latter has not been purified.

With other glucosides, products containing numerous methyl groups have been obtained.

Methylation with diazomethane is carried out in ethereal solution containing enough alcohol to dissolve the glucoside and at the ordinary temperature. Amorphous boron accelerates the change, but a much larger proportion of diazomethane is then required.

Pentamethylquercitrin is a pale yellow, amorphous powder.

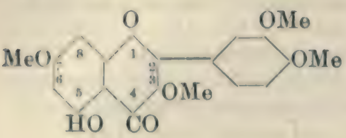
Tetramethylquercetin crystallises in colourless needles, m. p. 195—198°.

Tetramethylnorstrophantin forms a hygroscopic mass, m. p. below 100°. E. F. A.

Colourless Tetramethylquercetin. JOSEF HERZIG [and PAULA BÖTTCHER] (*Monatsh.*, 1912, 33, 683—699. Compare preceding abstract).—Colourless tetramethylquercetin is converted quantitatively by means of methyl iodide and potassium hydroxide, or of methyl sulphate, or of diazomethane into pentamethylquercetin.

By the action of diazomethane on quercetin this tetramethylquercetin is obtained in addition to pentamethylquercetin. It is accordingly an intermediate product of methylation, whereas previously the yellow

tetramethylquercetin (annexed formula), which does not react with diazomethane, had been suggested as the intermediate product of methylation.



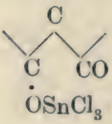
The hindrance of the ortho-hydroxyl group towards methylation with diazomethane is only made manifest when the other hydroxyl groups are substituted.

Although resistant towards diazomethane, the yellow tetramethylquercetin can be methylated either with potassium hydroxide and methyl iodide or methyl sulphate.

On methylation of quercitrin with diazomethane, a red coloration is obtained in the early stages, giving way to yellow. This is attributed to the influence of the hydroxyl groups in positions 3 and 5.

Colourless tetramethylquercetin is shown to be identical with 5 : 7 : 3′ : 4′-tetramethoxyflavonol (Kostanecki, Lampe, and Tambor, Abstr., 1904, i, 517).

Pfeiffer (Abstr., 1911, i, 595) has shown that hydroxyl groups in the ortho-position to the carbonyl group react with tin tetrachloride in benzene solution at the temperature of the water-bath, forming substitution compounds of the annexed type, whereas hydroxy-ketones with the hydroxyl groups in other positions only form additive compounds. It is now shown that such substitution compounds are given by 7-methyleuxanthone and by yellow tetramethylquercetin, whereas colourless tetramethylquercetin forms an additive product.



Quercetin crystallises with $2H_2O$, and is then soluble in ester; anhydrous quercetin is insoluble.

Monoacetyltetramethylquercetin, from the colourless tetramethylquercetin, crystallises in colourless needles, m. p. 160—163°.

The colourless tetramethylquercetin has a great tendency to become coloured, particularly on crystallisation; from acetic acid it crystallises in pale yellow needles. E. F. A.

Constitution of the Aloïns of the Natal Aloes. EUGÈNE LÉGER (*Compt. rend.*, 1912, **155**, 172—175. Compare Abstr., 1898, i, 445; 1899, i, 157, i, 820; 1902, i, 549, 685).—A further proof of the presence of nataloïn and homonataloïn in Natal aloes, the latter of which Tschirch and Klaveness were unable to find (compare Abstr., 1901, i, 399). Homonataloïn on suitable hydrolysis yields a sugar, which can be isolated through its phenylbenzylhydrazone, and by its properties shown to be *d*-arabinose. Nataloïn has not as yet been hydrolysed for its sugar, but as it, like homonataloïn, yields furfuraldehyde on distillation with dilute sulphuric acid, it is probable that the two aloïns have similar constitutions, and contain the same sugar. W. G.

Laserpitin. OTTO MORGENSTERN (*Monatsh.*, 1912, **33**, 709—749).—Laserpitin, $C_{26}H_{40}O_7$, obtained by extraction of colourless gentian root with light petroleum, forms rhombic crystals [$a:b:c$ =

0·47644 : 1 : 1·32865], m. p. 117—117·5° to a clear, colourless liquid, $[\alpha]_D^{18\cdot5} + 118\cdot7°$. The hydrochloride crystallises in octahedra, m. p. 135—136°. With bromine a crystalline bromide, $C_{26}H_{40}O_7Br_4$, is obtained, m. p. 163—165°. Laserpitin could not be acetylated, but it forms a crystalline acetate, $C_{26}H_{40}O_7,C_2H_4O_2$, which loses the acetic acid on drying in a vacuum at 80°. Laserpitin does not react with phenylhydrazine.

On reduction in acetic anhydride solution with zinc dust, the acetate of the corresponding alcohol is produced as an amorphous, reddish-yellow compound. In presence of colloidal palladium and hydrogen it is reduced to *tetrahydrolaserpitin*, $C_{26}H_{44}O_7$, which forms crystals, m. p. 92—96°.

Quantitative hydrolysis proves that laserpitin contains two angelic acid residues, and by the action of alkali hydroxide, laserol is converted by the opening of the lactone ring into an acid. The acid character of laserol was further established by the quantitative elimination of carbon dioxide. The readiness with which the lactone ring closes again is in favour of its being a γ-lactone. The hydroxyl groups in laserol were identified by the preparation of *diacetyl-laserol*, an amorphous, reddish-yellow substance.

By the action of phenylhydrazine, a *phenylhydrazone* of laserol is formed, m. p. about 92°; this is a reddish-brown, amorphous powder. The keto-group was also identified by reduction and determination of the active hydrogen in dihydrolaserol by the method of Zerewitinoff.

The parent hydrocarbon could not be obtained by the action of hydrogen iodide and phosphorus.

On oxidation of laserol, formic acid and *γ-hydroxy-δ-methylheptanoic acid* were obtained, the latter acid yielding α-methylbutyric, succinic, and malonic acids on oxidation. γ-Hydroxy-δ-methylheptanoic acid is an amorphous, yellow powder, m. p. 95—100°, decomp. 142—145°.

To sum up, laserpitin contains two hydroxyl groups esterified with angelic acid, a lactone ring, a keto-group, and the carbon atoms are present in open chains. The position of the keto-group and one hydroxyl is fixed by the discovery of the hydroxymethylheptanoic acid. E. F. A.

The Composition of Picrotoxinin. PAUL HORRMANN (*Ber.*, 1912, **45**, 2090—2095).—The author finds that picrotoxinin has the composition $C_{14}H_{16}O_6$, instead of $C_{15}H_{16}O_6$, as previously stated (E. A. Schmidt, Abstr., 1884, 845; Barth and Kretschy, Abstr., 1884, 846).

Bromopicrotoxinin (Meyer and Bruger, Abstr., 1899, i, 226), obtained by the action of bromine water on picrotoxinin, is a mixture of two isomerides, α-bromopicrotoxinin, prisms, decomposing at 290°, $[\alpha]_D^{17} - 69°9'$ (in chloroform), and β-picrotoxinin, needles, decomposing at 280°, $[\alpha]_D^{17} - 129°14'$ (in chloroform); the two constituents of the mixture in which the β-isomeride preponderates can be separated by fractional crystallisation from acetic acid, and subsequently from alcohol. Both isomerides are reduced in alcoholic solution by zinc dust and ammonium chloride to pure picrotoxinin, $C_{14}H_{16}O_6$ (not previously obtained pure), anhydrous needles, m. p. 20 ·5°, or some-

times prisms with water of crystallisation ($\frac{1}{2}H_2O$), $[\alpha]_D^{17}$ +4°40′ (in alcohol), +4°5′ (in acetone) (compare Meyer and Bruger, *loc. cit.*). Bromination of pure picrotoxinin gives the same mono-substitution product as does the ordinary substance obtained directly from picrotoxin. D. F. T.

Chlorophyll. XX. The Two Components of Chlorophyll. RICHARD WILLSTÄTTER and MAX ISLER (*Annalen*, 1912, **390**, 269—339).—Previous investigations have shown that two, and only two, fission products, namely, phytochlorin-*e* and phytorhodin-*g*, are obtained by the successive action of acids and alkalis on the chlorophyll of all plants examined, whether marine or land plants. These two products are obtained in approximately constant proportions, namely, 1 mol. of the phytorhodin to, at most, about 2·5 mols. of the phytochlorin. By the partition method with petroleum and aqueous methyl alcohol, the authors have separated chlorophyll into a bluish-green or greenish-blue chlorophyll-*a* and a yellowish-green chlorophyll-*b*; the former yields only phytochlorin-*e*, and the latter only phytorhodin-*g*, by fissive decomposition. These two components of chlorophyll are shown to be free from colourless or coloured concomitants and also from transformation products resulting by allomerisation.

Phæophytin is also shown to be a mixture of the two corresponding magnesium-free components. Usually, the proportion of these two components in phæophytin is the same as that in chlorophyll, namely, 1 mol. of component *b* to 2·5 mols. of component *a*. Some exceptions have been observed; phæophytin preparations from *Pinus* and from sage are richer in component *b*.

The proportion of the two components in chlorophyll, therefore, has been carefully examined, with results which show that the following precautions must be taken in order to obtain an accurate estimation. (1) During the extraction of the chlorophyll from the leaves, a fractional separation of the two components may occur. It is necessary, therefore, quantitatively to extract the colouring matter from the leaves. (2) According to the dilution of the extract and its content of water and of impurities, the phæophytin separates more or less incompletely; the portion remaining in the solution is richer in component *a*. It is necessary, therefore, that the chlorophyll in the extract shall be converted quantitatively into phæophytin before hydrolysis.

In estimating the proportion of the components *a* and *b* of the chlorophyll of any plant, therefore, the successive processes are complete extraction of the colouring matter, conversion without loss into crude phæophytin, isolation of the latter and its hydrolysis, as smoothly as possible, and finally the quantitative separation of the mixture of phytochlorin-*e* and phytorhodin-*g*. Since the chlorophyll of suitable plants can be converted into phytochlorin-*e* and phytorhodin-*g* without the formation of by-products, the amounts of the components, *a* and *b*, of chlorophyll can be estimated by determining colorimetrically the amounts of phytochlorin-*e* and phytorhodin-*g* produced therefrom, by comparison with standard solutions of the

pure substances. By the process indicated above, the authors have commenced an investigation of the proportions of the components *a* and *b* in the chlorophyll of many plants; the proportion is generally nearly constant, the mean of twenty-four experiments being 2·5 : 1 with an average variation from the mean of 10%. (Incidentally it has been shown that chlorophyll constitutes 0·7—1% of the dried leaves.)

It is necessary that the total chlorophyll extracted from the leaf, not just the portion which separates in the form of phæophytin, shall be converted into phytochlorin-*e* and phytorhodin-*g* by successive treatment with acid and alkali. The omission to fulfil this condition explains why other investigators have recorded such varying values of the proportions of the constituents of chlorophyll.

The necessity of quantitatively converting the chlorophyll in an extract into phæophytin and subsequently treating with concentrated alkali introduces disadvantages. In order to isolate the whole of the phæophytin, it is necessary to isolate as well a large amount of the accompanying substances. These substances, some of which are themselves hydrolysable, hinder the complete hydrolysis of the phæophytin, even under energetic treatment. The formation of phytochlorin-*e* and phytorhodin-*g* is not a simple process. After passing through the brown phase, the substance suffers hydrolysis, easily at the phytyl group, with difficulty at the β-CO_2Me group. If the last hydrolysis is incomplete, the normal products of fission, phytochlorin-*e* and phytorhodin-*g*, are accompanied by more feebly basic derivatives. In addition to this, abnormal phytochlorins and phytorhodins may be produced through allomerism of the chlorophyll. Starting with pure phæophytin, the smooth course of the fission is easily controlled, because in a properly conducted experiment the sum of the phytochlorin-*e* and phytorhodin-*g* represents approximately two-thirds of the phæophytin. This control is impossible when an unknown amount of phæophytin is hydrolysed by alkali; in such circumstances, the only clue to a properly conducted hydrolysis is the production of the more feebly basic derivatives only in slight amount.

The complete extraction of the chlorophyll from the leaf is effected by alcohol, by percolation in the case of the powdered dry leaf, by digestion and decantation in the case of the fresh leaf. In order to prevent allomerisation of the chlorophyll, the alcoholic extract is added at once to aqueous-alcoholic oxalic acid. Water is added, and the phæophytin is extracted completely by ether. After the evaporation of the ether in a vacuum, the residual crude phæophytin, in quantities of about 0·3—0·6 gram, is dissolved in 1 c.c. of pyridine, heated on the water-bath, treated with 5—10 c.c. of boiling methyl-alcoholic potassium hydroxide, and then boiled for one minute over a naked flame. This treatment is necessary to hydrolyse completely the phæophytin, and at the same time to reduce to a minimum the decomposition of the phytorhodin-*g* by the alcoholic alkali. The solution is acidified and extracted with ether. The ethereal solution is extracted with 12% hydrochloric acid to separate the chlorins and rhodins from accompanying colourless or yellow impurities. The

12% hydrochloric acid extract is neutralised and shaken with ether. The ethereal solution is treated with 3% hydrochloric acid to remove the bulk of the phytochlorin, then with 5% hydrochloric acid, and finally with 9% hydrochloric acid to extract the phytorhodin. For details the paper must be consulted, but the final result is that the phytochlorin-*e* is obtained in 3% hydrochloric acid and the phytorhodin-*g* in 9% hydrochloric acid. These solutions are made up to volume with hydrochloric acid of the same strength (saturated with ether), and are compared in a Duboscq colorimeter with standard solutions of phytochlorin-*e* ($C_{34}H_{36}O_6N_4$) and of phytorhodin-*g* ($C_{34}H_{34}O_7N_4$) containing 1/20,000 mol. per litre. The results of numerous experiments show that, whether the fresh or the dried leaf is examined, the proportion of phytochlorin-*e* to phytorhodin-*g*, obtained from the chlorophyll of different plants, or from the chlorophyll of one and the same plant under different conditions of growth, is approximately constant, averaging 2·5 to 1.

The method whereby the components *a* and *b* of chlorophyll (from the leaf of the stinging-nettle) have been separated depends on the systematic fractional partition of the chlorophyll between aqueous methyl alcohol and petroleum; chlorophyll-*b* is obtained in the alcoholic layer, chlorophyll-*a* in the petroleum. The original paper must be consulted for details of the separation and purification.

Chlorophyll-a (*Phytylchlorophyllide*-a),

$$[C_{32}H_{30}ON_4Mg](CO_2Me)(CO_2\cdot C_{20}H_{39}),\tfrac{1}{2}H_2O,$$

is a bluish-black, microcrystalline powder, which sinters and forms a viscous mass at 117—121°. It dissolves very easily in most solvents, but is very sparingly soluble in petroleum of b. p. 30—50°. The purity of the substance is guaranteed by the pure yellow colour obtained in the "phase" test, and by the fact that its fissive decomposition yields phytochlorin-*e*, but no other phytochlorins or phytorhodins. An ethereal solution of the substance is decomposed, gradually by 6%, instantly by 20%, hydrochloric acid. An excess of ethereal hydrogen chloride produces at once the blue colour of a phæophytin hydrochloride.

Chlorophyll-b (*Phytylchlorophyllide*-b),

$$[C_{32}H_{28}O_2N_4Mg](CO_2Me)(CO_2\cdot C_{20}H_{39}),$$

is a dark green or greenish-black, glistening, microcrystalline powder, which sinters at 86—92°, and becomes viscous at 120—130°. It is, as a rule, somewhat less soluble than chlorophyll-*a*, but is quite insoluble in cold petroleum. It develops a transient, brilliant red coloration in the "phase" test, and yields by treatment with boiling alcoholic potassium hydroxide phytorhodin-*g* accompanied by a trace of phytochlorin-*e*. In ethereal solution it is converted into the phæophytin, slowly by 15%, rapidly by 20%, hydrochloric acid; ethereal hydrogen chloride produces instantly a green solution of the phæophytin hydrochloride.

Phæophytins *a* and *b* can be obtained by the addition of alcoholic oxalic acid to suitable solutions obtained during the separation of chlorophylls *a* and *b* as above.

A separation can also be effected by Willstätter and Stoll's method

of fractional extraction with hydrochloric acid. The chlorophyll is extracted from the leaf and converted into phæophytin. A 0·25% ethereal solution of the latter is shaken with 27% hydrochloric acid, and finally with 29% hydrochloric acid, to remove the last trace of phæophytin-*a*. The ethereal solution is concentrated until phæophytin-*b* begins to separate. The hydrochloric acid extracts contain phæophytin-*a*, but since a partial hydrolysis of the phytyl group occurs, it is best to keep the extracts until the hydrolysis is complete and to isolate the *a*-component in the form of phæophorbide-*a*.

The separation of phæophytin-*a* and -*b* by Marchlewski's process with zinc hydroxide is incomplete, and yields products which are not free from ash.

Phaeophytin-a (*Phytylphaeophorbide*-a),

$$[C_{32}H_{32}ON_4](CO_2Me)(CO_2{\cdot}C_{20}H_{39}),\tfrac{1}{2}H_2O,$$

forms bluish-black, waxy lumps, which sinter at 110—114° and become viscous at 120°. It is deposited from hot alcoholic solution in microcrystalline aggregates. Concentrated solutions are olive-brown; dilute solutions are olive-green, similar to those of phytochlorin-*e*, but differing in exhibiting a faint red fluorescence. In glacial acetic acid, phæophytin-*a* (and, so also, the *b*-component) forms intensely blue or green complex metallic compounds with the acetates of copper, zinc, and other metals. Phæophytin-*a* gives a yellow phase with concentrated methyl-alcoholic potassium hydroxide, changing to green owing to the formation of a complex in which potassium exercises the function of the magnesium in chlorophyll. Phæophytin-*a* resembles methylphæophorbide in most respects, but has weaker basic properties; it is extracted from ethereal solution partly by 29%, almost completely by 32%, hydrochloric acid.

Phaeophytin-b (*Phytylphaeophorbide*-b),

$$[C_{32}H_{30}O_2N_4](CO_2Me)(CO_2{\cdot}C_{20}H_{39}),$$

is obtained as a greenish-black mass, more brittle than the *a* component. It sinters at 148—152°, becomes viscous, and decomposes at 160—170°. It gives a fine red, transient phase with concentrated alcoholic potassium hydroxide, and yields only phytorhodin-*g* by fissive hydrolysis. The basic properties of phæophytin-*b* are much weaker than those of component *a*; it is extracted only incompletely from ethereal solution by 35% hydrochloric acid.

[With E. Hug.]—Chlorophyllan has been prepared from grass according to the instructions of Hoppe-Seyler. By partial solution in petroleum it is shown to be a mixture containing fats, lecithin, and other substances. According to the authors, chlorophyllan is simply chlorophyll which has been decomposed by plant acid, and more or less extensively allomerised by the action of solvents. C. S.

Tannic Acid, Ethyl Gallate, and the Supposed Ester of Tannic Acid. Henry C. Biddle and W. P. Kelley (*J. Amer. Chem. Soc.*, 1912, **34**, 918—923).—It is considered that the optical activity of tannic acid may be due to the presence of dextrose, either as an impurity or as an essential part of the substance in some combination of the nature of a glucoside. It has been found that on decomposing the dextrose by fermentation with yeast, the optical activity is com-

pletely destroyed without the whole of the tannic acid being hydrolysed to gallic acid.

The supposed ethyl tannate (m. p. 157°) described by Manning (Abstr., 1910, i, 851) has been prepared in accordance with his directions, and has proved to be identical with ethyl gallate.

Ethyl gallate begins to sinter at about 145°, and melts to a turbid liquid at 149—150°, which becomes clear at 157—158°. A study of this ester has shown that it probably exists in two crystalline forms, one consisting of hair-like needles, stable at the ordinary temperature, and the other, flat plates, stable at higher temperatures, and that the turbid condition of the fused ester is due to the presence of some of the needles. E. G.

Spirans. II. Detection of the Special Asymmetry Caused by the Spiran Carbon Atom. Hermann Leuchs and Erich Gieseler (*Ber.*, 1912, **45**, 2114—2129. Compare this vol., i, 179).—It has been shown that bicyclic spirans can be regarded as derived from disubstituted malonic acids by double ring closure between the carboxyl groups and the two substituents. Such spirans are molecular asymmetric in consequence of the perpendicularity of the two planes in which lie the two rings which have the spiran carbon atom in common.

If one or both of the C:C groups in an allene of the type $Cab{=}C{=}Ccd$ be replaced by a cyclic group, the configurations of the resulting substances are represented, for example, by

$$\begin{matrix}a\\b\end{matrix}\!>\!C\!<\!\begin{matrix}[CH_2]_x\\ [CH_2]_x\end{matrix}\!>\!C{=}C\!<\!\begin{matrix}c\\d\end{matrix} \quad\text{and}\quad \begin{matrix}a\\b\end{matrix}\!>\!C\!<\!\begin{matrix}[CH_2]_x\\ [CH_2]_x\end{matrix}\!>\!C\!<\!\begin{matrix}[CH_2]_x\\ [CH_2]_x\end{matrix}\!>\!C\!<\!\begin{matrix}c\\d\end{matrix}.$$

(Dotted lines represent bonds in a plane perpendicular to the plane of the paper.)

The molecular asymmetry of the former type of substance has been proved by the resolution of 1-methyl*cyclo*hexylidene-4-acetic acid by Perkin, Pope, and Wallach. Substances of the second type are bicyclic spirans, such as those mentioned above. Experiments on the resolution of such snbstances (or, rather, on substances in which *c* and *d* are the same as *a* and *b*, in order that there may be no question as to the true molecular asymmetry of the substances) are in progress.

The present communication, however, deals with another method whereby the asymmetry conditioned by the spiran carbon atom may be at least indicated, if not proved. If a substance contains *n* "asymmetric" atoms, the number of stereoisomerides, x, is in general given by the equation $x=2^n$; therefore, if x is known, n can be calculated. The authors' experiments deal with the bis-γ-lactone-*aa*-spirans. The simplest member of this class is *bis-γ-butyrolactone-aa-spiran*, $\begin{matrix}\overset{*}{C}H_2\cdot CH_2\\ |\qquad\quad\\ O\text{——}CO\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot\overset{*}{C}H_2\\ \qquad\quad |\\ CO\text{—}O\end{matrix}$, m. p. 109—110°, hexagonal plates, which is obtained in 11% yield by the interaction of sodium ethoxide, ethyl malonate, and β-bromoethyl acetate. This compound is unsuited for the purpose in question, since it does not contain "asymmetric" carbon atoms. (It is obtained in too small quantity

for its resolution [or that of an acid derived therefrom] to be effected by the usual methods). If, however, two similarly situated carbon atoms (those marked by an asterisk) are made equally asymmetric, and if these two atoms are the only sources of asymmetry in the molecule, the substance should exist in two inactive modifications, internally and externally compensated respectively. If, in addition, asymmetry is conditioned by the spiran carbon atom, then the substance should exist in three racemic forms. (Only three racemic modifications are possible in consequence of the symmetrical constitution of the substance. Diagrams are given of models whereby this point is made clear.) Substances of the required type are bis-γ-valerolactone-$\alpha\alpha$-spiran, $\begin{array}{l}\mathrm{CHMe{\cdot}CH_2}\\ |\\ \mathrm{O{-\!-\!-}CO}\end{array}\!\!>\!\mathrm{C}\!<\!\!\begin{array}{l}\mathrm{CH_2{\cdot}CHMe}\\ \qquad\quad |\\ \mathrm{CO{-}O}\end{array}$, and bis-$\delta$-bromo-$\gamma$-valerolactone-$\alpha\alpha$-spiran, $\mathrm{CH_2Br{\cdot}CH}\!<\!\!\begin{array}{l}\mathrm{CH_2-}\\ \mathrm{O{\cdot}CO}\end{array}\!\!>\!\mathrm{C}\!<\!\!\begin{array}{l}\mathrm{CH_2-}\\ \mathrm{CO{\cdot}O}\end{array}\!\!>\!\mathrm{CH{\cdot}CH_2Br}$, obtained by Fittig and Hjelt (Abstr., 1883, 456) by the action of hydrogen bromide or of bromine on diallylmalonic acid or its ester. Fittig and Hjelt describe only one product, m. p. 130°, in the case of the brominated spiran. The authors show that this is a mixture; by working under somewhat different conditions, they have isolated the three isomerides required to substantiate their theory. The action of bromine on ethyl diallylmalonate in chloroform at 0—15° yields, in addition to a considerable quantity of an oil, 61·5% of crystalline product, which is separated, by fractional solution in and crystallisation from various solvents, into three isomeric *bis-δ-bromo-γ-valerolactone-$\alpha\alpha$-spirans*, having m. p. 156—158°, 108—110°, and 153—154·5° respectively. The oil is shown to consist of the *lactone*,

$$\mathrm{CH_2Br{\cdot}CH}\!<\!\!\begin{array}{l}\mathrm{-CH_2}\\ \mathrm{O{\cdot}CO}\end{array}\!\!>\!\mathrm{C(CO_2Et){\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br},$$

by analysis and by the fact that at 160—170° it decomposes into ethyl bromide and a mixture of the preceding lactonespirans. These lactonespirans are also produced by the bromination of diallylmalonic acid in ether or glacial acetic acid.

The preceding three lactonespirans are represented as γ-lactones, because by prolonged treatment with concentrated aqueous ammonia they are converted into piperidine derivatives, not into pyrrolidine derivatives as would be the case if the substances were δ-lactones. Thus, bis-δ-bromo-γ-valerolactone-$\alpha\alpha$-spiran, m. p. 158°, is converted into two isomeric *bis-5-hydroxy-2-piperidone-3 : 3-spirans*,

$$\mathrm{CH_2}\!<\!\!\begin{array}{l}\mathrm{CH(OH){\cdot}CH_2}\\ \mathrm{NH{-\!-\!-\!-}CO}\end{array}\!\!>\!\mathrm{C}\!<\!\!\begin{array}{l}\mathrm{CH_2{\cdot}CH(OH)}\\ \mathrm{CO{-\!-\!-\!-}NH}\end{array}\!\!>\!\mathrm{CH_2},$$

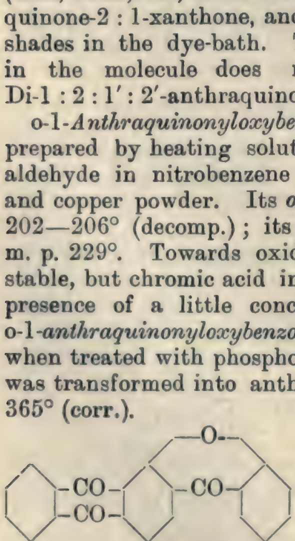
one of which has m. p. 260° (decomp.), and is sparingly soluble in water, whilst the other is easily soluble and has m. p. 245° (decomp.). The lactonspiran, m. p. 153—154·5°, yields the former of these piperidine derivatives by treatment with ammonia; probably also the latter is produced, but the amount of material available is too small for its isolation. The lactonespiran, m. p. 108—110°, yields only one *bis-5-hydroxy-2-piperidone-3 : 3-spiran*, m. p. 235° (decomp.).

The behaviour of the three racemic lactonespirans with ammonia can be utilised to throw some light on their configurations. The

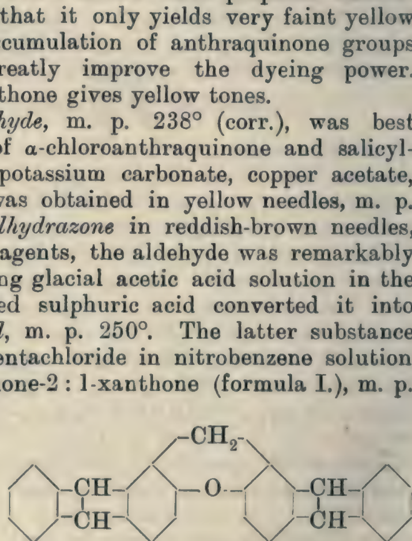
configurations may be represented thus: $\begin{pmatrix} d\,d & l\,l \\ \vee & \vee \\ d & l \end{pmatrix}$, $\begin{pmatrix} d\,d & l\,l \\ \vee & \vee \\ l & d \end{pmatrix}$ and $\begin{pmatrix} l\,d & d\,l \\ \vee & \vee \\ l & d \end{pmatrix}$. During the conversion of the lactonespirans into hydroxypiperidonespirans, the lactone rings are ruptured, and consequently the asymmetry conditioned by the spiran carbon atom disappears. The lactonespirans having the first two configurations, therefore, yield the same intermediate product, $(CO_2H)_2C[CH_2{\cdot}CH(OH){\cdot}CH_2Br]_2$, from which, by replacement of the bromine atoms by NH_2-groups and subsequent elimination of water, two isomeric bishydroxypiperidonespirans are produced, the configurations of which are represented by $\begin{pmatrix} d\,d & l\,l \\ \vee & \vee \\ d & l \end{pmatrix}$ and $\begin{pmatrix} d\,d & l\,l \\ \vee & \vee \\ l & d \end{pmatrix}$. The lactonespiran having the third configuration given above can form only one bishydroxypiperidonespiran, the configuration of which is represented by $\begin{pmatrix} l\,d & d\,l \\ \vee & \vee \\ l & d \end{pmatrix}$. This lactonespiran, therefore, is the one which has m. p. 108—110°. The other two lactonespirans have, each, one or other of the two remaining configurations. C. S.

Anthraquinonexanthones. FRITZ ULLMANN and DEZSÖ ÜRMÉNYI (*Ber.*, 1912, **45**, 2259—2272).—The authors have prepared anthraquinone-2 : 1-xanthone, and find that it only yields very faint yellow shades in the dye-bath. The accumulation of anthraquinone groups in the molecule does not greatly improve the dyeing power. Di-1 : 2 : 1′ : 2′-anthraquinonexanthone gives yellow tones.

o-1-*Anthraquinonyloxybenzaldehyde*, m. p. 238° (corr.), was best prepared by heating solutions of α-chloroanthraquinone and salicylaldehyde in nitrobenzene with potassium carbonate, copper acetate, and copper powder. Its *oxime* was obtained in yellow needles, m. p. 202—206° (decomp.); its *phenylhydrazone* in reddish-brown needles, m. p. 229°. Towards oxidising agents, the aldehyde was remarkably stable, but chromic acid in boiling glacial acetic acid solution in the presence of a little concentrated sulphuric acid converted it into o-1-*anthraquinonyloxybenzoic acid*, m. p. 250°. The latter substance when treated with phosphorus pentachloride in nitrobenzene solution was transformed into anthraquinone-2 : 1-xanthone (formula I.), m. p. 365° (corr.).



(I.)



(II.)

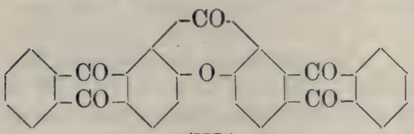
2 : 2′-*Dihydroxy*-1 : 1′-*dianthracylmethane*, m. p. 240—242° (corr., decomp.), was obtained by the action of aqueous formaldehyde on 2-hydroxyanthracene in acetic acid or in alkaline solution. Its *diacetyl* derivative has m. p. 232° (corr.). ms-*Methyl*-1 : 2 : 1′ : 2′-*dianthracenexanthen*, m. p. 274° (corr.), was similarly prepared by the

condensation of 2-hydroxyanthracene and acetaldehyde in glacial acetic acid solution in the presence of a few drops of concentrated hydrochloric acid. ms-*Phenyl*-1 : 2 : 1′ : 2′-*dianthracenexanthen*, obtained similarly, had m. p. 278° (corr.), and separated from benzene with $1C_6H_6$.

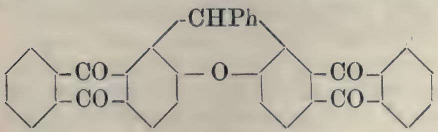
1 : 2 : 1′ : 2′-*Dianthracenexanthen* (formula II.) was readily prepared by the action of phosphoryl chloride on dihydroxydianthracylmethane in boiling xylene solution. It forms yellow needles, m. p. 322—323° (corr.).

1 : 2 : 1′ : 2′-*Dianthraceneacridine*, m. p. 348—349° (corr.), was obtained by heating dihydroxydianthracylmethane with ammonia during eight to ten hours at 215—225°. Oxidation with chromic acid in boiling glacial acetic acid solution converted it into 1 : 2 : 1′ : 2′-*dianthraquinoneacridine*, which did not melt below 440°.

2 : 2′-*Diacetoxy*-1 : 1′-*dianthraquinonylmethane*, m. p. 246° (corr.), was obtained by the oxidation of diacetoxydianthracylmethane by means of chromic acid. It was converted into 2 : 2′-*dihydroxy*-1 : 1′-*dianthraquinonylmethane* by alcoholic potassium hydroxide. The crystals evolved gas and blackened between 290° and 315°, and, after melting, immediately resolidified. The diacetyl derivative when heated with acetamide was transformed into *dianthraquinonexanthen*, which did not melt at 425°. Oxidation with chromic acid transformed it into 1 : 2 : 1′ : 2′-*dianthraquinonexanthone* (formula III.), m. p. 425°, which was, however, more readily obtained by oxidation of *ms*-methyldianthracenexanthen.



(III.)



(IV.)

ms-*Phenyl*-1 : 2 : 1′ : 2′-*dianthraquinonexanthen* (formula IV.), m. p. 378°, was obtained by the oxidation of *ms*-phenyl-1 : 2 : 1′ : 2′-dianthracenexanthen by excess of chromic acid in glacial acetic acid solution.

H. W.

Action of Hydrogen Peroxide on Acetothienone and α-Thiophenic Acid. MAURICE LANFRY (*Compt. rend.*, 1912, **155**, 170—172).—Acetothienone and thiophenic acid are both decomposed by hydrogen peroxide, very slowly in the cold, but much more rapidly on heating, the only products obtainable being sulphuric acid and an orange-yellow, resinous liquid. The proportion of acetothienone decomposed increases with the time of the reaction, the quantity of active oxygen, and the concentration of the hydrogen peroxide. No trace of either thienylglyoxylic or thiophenic acids could be detected in the residue (compare Holleman, Abstr., 1904, i, 474). Thiophenic acid behaves in a similar manner towards hydrogen peroxide, except that it is more resistant to the diluted reagent. W. G.

Rearrangement of Quinine by Sulphuric Acid. II. BRUNO BÖTTCHER and STEPHANIE HOROVITZ (*Monatsh.*, 1912, **33**, 567—582. Compare Abstr., 1911 i, 1011).—The optimum yield of α- and β-*iso*-

quinine, formerly described as bases *A* and *B*, is obtained by heating quinine with sulphuric acid (D 1·61) at 100° for three hours. When carefully purified, *a-iso*quinine has m. p. 196·5° (corr.), $[\alpha]_D - 245°$; *β-iso*quinine has m. p. 189° (corr.), $[\alpha]_D - 192°$. The salts of *a-iso*-quinine have a blue fluorescence in aqueous solution; the *platinichloride* crystallises in red, well formed, rhombic prisms; the *oxalate* crystallises in octahedra; the *hydrochloride*, $+\frac{1}{3}H_2O$, forms colourless needles. The following salts of *β-iso*quinine are described: the *oxalate*, $3H_2O$, crystallises in bunches of needles; the *sulphate*, $6H_2O$, forms colourless needles; the *hydrochloride*, $\frac{1}{3}H_2O$, also forms needles; the *platinichloride*, yields reddish-yellow, rhombic prisms.

Both *a*- and *β-iso*quinine as well as nichine are formed on the rearrangement of quinine by hydrogen iodide; Skraup described the mixture of the two bases as *ψ*-quinine; Lippmann obtained *β-iso*-quinine only. E. F. A.

Cinchona Alkaloids. XVI. Preliminary Synthetic Experiments. PAUL RABE (*Ber.*, 1912, **45**, 2163—2171).—[With RICHARD PASTERNACK.]—The reaction between magnesium benzyl chloride and ethyl cinchonate in ether leads to the formation of *γ-quinolyl benzyl ketone*, $C_9NH_6 \cdot CO \cdot CH_2Ph$, m. p. 91°, and *γ-quinolyl-dibenzylcarbinol*, $C_9NH_6 \cdot C(CH_2Ph)_2 \cdot OH$, m. p. 163—164°. The former yields a *picrate*, m. p. 192°, *methiodide*, m. p. 162—164°, *oxime*, the *hydrochloride* of which has m. p. 245°, and *oximino*-compound,

$$C_9NH_6 \cdot CO \cdot CPh \colon NOH,$$

m. p. 216° (decomp.).

[With THEODOR HUNNIUS].—Certain *αβ*-oximino-ketones can be reduced directly to the hydramines by the Paal-Skita method; thus in the presence of colloidal palladium, a solution of oximinodeoxybenzoin in alcohol and hydrochloric acid is reduced by hydrogen, under a pressure of 2 atmospheres, to *β*-amino-*αβ*-diphenylethyl alcohol. In a similar manner, oximinophenyl ethyl ketone is reduced to *β*-amino-*a*-phenylpropyl alcohol, *β-oximino-a-phenylpropyl alcohol*,

$$NOH \colon CMe \cdot CHPh \cdot OH,$$

m. p. 112°, being obtained as a by-product.

[With PETER RIEPER.]—The partial synthesis of cinchonine from cinchotoxine depends on the fact that *N*-bromocinchotoxine, under the influence of sodium ethoxide, loses hydrogen bromide with the formation of the bicyclic quinuclidine ring. The following reactions are of the same type. Deoxybenzoin and sodium ethoxide in alcoholic solution react with *N*-chlorodimethylamine to form *phenyl a-dimethyl-aminobenzyl ketone*, $NMe_2 \cdot CHPh \cdot COPh$, b. p. 193°/15 mm., a greenish-yellow, viscous liquid, having a characteristic odour (*methiodide*, m. p. 153°, *hydrochloride*, m. p. 206—210° [decomp.], *platinichloride*, decomp. 199°, *picrate*, decomp. 148°, *picrolonate*, m. p. 174°, decomp. 180°), and with *N*-chloropiperidine to form *phenyl a-piperidylbenzyl ketone*, $C_5NH_{10} \cdot CHPh \cdot COPh$, m. p. 82°, prisms (*methiodide*, m. p. 182°).

[With ERNST MILARCH].—Sodioformylacetone and ethyl aceto-acetate were brought into reaction with alcoholic ammonia, and the solution was subsequently treated with glacial acetic acid, in the hope

of preparing a derivative of 4-acetonyldihydropyridine. However, the chief product of the reaction is *ethyl* 2:6-*dimethylpyridine-3-carboxylate*, $C_{10}H_{13}O_2N$, b. p. 244—245° or 129—130°/18 mm., D_4^{20} 1·060, n_D^{20} 1·5070, which forms a *picrate*, m. p. 137°, and *picrolonate*, m. p. 142° (decomp.). C. S.

Creatinine and its Oximes. Ernst Schmidt (*Arch. Pharm.*, 1912, **250**, 330—381).—The action of nitrous acid on creatinine yields, not nitrosocreatinines as might be expected, but the oxime of methylhydantoin, together with creatinineoxime as by-product. The mixture is separated by warm alcohol, in which the latter is almost insoluble.

The composition of the methylhydantoinoxime is proved by the analysis of the substance and of its silver derivative, by its hydrolysis by warm hydrochloric acid to hydroxylamine and methylparabanic acid, and by the formation of the substance from methylhydantoin and alkaline sodium nitroprusside.

[With Eugen Thumann.]—Creatinine dissolved in nitric acid, D 1·140, reacts with solid sodium nitrite at 0° to form the *oxime* of methylhydantoin, $\mathrm{NOH{:}C}<\begin{matrix}\mathrm{CO-NH}\\ \mathrm{NMe\cdot CO}\end{matrix}$, m. p. 193—194° (decomp.), colourless needles. The oxime has feebly acidic, but no basic, properties, does not respond to the Liebermann test, and yields hydroxylamine by treatment with boiling hydrochloric acid. It reacts with silver nitrate in aqueous solution to form a *silver* derivative, $C_4H_6O_4N_3Ag$, the oxime having combined with the elements of water and changed to the oxime of methylhydantoic acid during the reaction. Methylhydantoinoxime reacts with hot aqueous phenylhydrazine hydrochloride and sodium acetate to form *methylhydantoin-phenylhydrazone*, $\mathrm{NHPh\cdot N{:}C}<\begin{matrix}\mathrm{NMe\cdot CO}\\ \mathrm{CO-NH}\end{matrix}$, m. p. 238—240°, green needles, and reacts with boiling acetic anhydride to form the *diacetyl* derivative, $\mathrm{NOAc{:}C}<\begin{matrix}\mathrm{CO-NAc}\\ \mathrm{NMe\cdot CO}\end{matrix}$, m. p. 186°, colourless leaflets.

By evaporation with hydrochloric acid, methylhydantoinoxime is decomposed into hydroxylamine and methylparabanic acid. This acid and ammonia are produced by the reduction of the oxime by sodium amalgam and dilute acetic acid.

Methylhydantoinoxime is decomposed by boiling barium hydroxide, yielding ammonia, methylamine, and carbonic and oxalic acids. By treatment with alkaline potassium permanganate at 60°, the oxime is converted into a substance, $C_4H_5O_3N_3$, which appears to be isomeric with the oxime, but does not exhibit similar properties; it does not melt at 270°, does not react with hydrochloric acid or with phenylhydrazine, but does form an amorphous *silver* derivative. Its constitution is as yet undetermined.

[With W. Hennig.]—*Creatinineoxime*, $\mathrm{NH{:}C}<\begin{matrix}\mathrm{NMe\cdot C{:}NOH}\\ \mathrm{NH-CO}\end{matrix}$, white needles, darkening at 250°, agrees in its properties and behaviour with Kramm's nitrosocreatinine obtained by the action of alkaline sodium

nitroprusside on creatinine (Abstr., 1899, i, 85). The following experiments, however, prove that the substance is really an oxime not a nitroso-compound. It forms a *silver* derivative,

$$2C_4H_5O_2N_4Ag,H_2O,$$

platinichloride, $2C_4H_6O_2N_4,H_2PtCl_6$, and aurichlorides of different composition and m. p., reacts with hydrochloric acid under different conditions to form a *hydrochloride*, $C_4H_6O_2N_4,HCl,H_2O$, decomp. 200—205°, or methylparabanic acid, hydroxylamine, and ammonia, or ammonium tetra-oxalate, hydroxylamine, ammonia, and methylamine. Creatinineoxime yields a *diacetyl* derivative, m. p. 210°, by acetylation, is reduced to methylguanidine by tin and hydrochloric acid, and is converted into methylhydantoinoxime by sodium nitrite and nitric acid, D 1·140, at 0°. Unsuccessful attempts have been made to prepare nitrosocreatinine from nitrososarcosine and cyanamide, and from nitrous fumes and aqueous creatinine. C. S.

Constitution of Morphine. Conversion of the Methyl Ethers of α- and ε-Methylmorphimethine into 3:4:6- and 3:4:8-Trimethoxyphenanthrene respectively. ROBERT PSCHORR [with F. DICKHÄUSER and C. D'AVIS] (*Ber.*, 1912, **45**, 2212—2220).—The methyl ether of bromoacetoxydihydro-α-methylmorphimethine when treated with acetic anhydride is transformed into 4-acetoxy-3:6-dimethoxyphenanthrene, whilst, under similar conditions, the methyl ether of bromohydroxydihydro-ε-methylmorphimethine yields 4-acetoxy-3:8-dimethoxyphenanthrene. The proof so obtained that the secondary alcoholic hydroxyl group of ψ-codeine is attached to the C-atom 8 of the phenanthrene nucleus, considered in conjunction with Knorr's proof of the similar structure of codeine (morphine) and ψ-codeine, renders the formula for morphine proposed by Pschorr (Abstr., 1903, i, 193) untenable, but supports that advanced by Knorr and Hörlein (Abstr., 1907, i, 789).

Bromohydroxydihydro-α-methylmorphimethine methyl ether, m. p. 112° (corr.), was obtained by the bromination of α-methylmorphimethine methyl ether in chloroform solution and treatment of the reaction product with water and ether. Its *acetyl* derivative, m. p. 126° (corr.), was formed when α-methylmorphimethine methyl ether was brominated in glacial acetic acid solution in the presence of sodium acetate, and had $[\alpha]_D^{26}$ +108·4° in methyl-alcoholic solution. When the latter was boiled with acetic anhydride, it was transformed into 4-acetoxy-3:6-dimethoxyphenanthrene, which was further identified by means of its picrate.

Attempts to brominate ε-methylmorphimethine methyl ether in glacial acetic acid did not lead to a crystalline product. Bromination in chloroform solution, followed by treatment with water and sodium hydroxide, yielded *bromohydroxy-ε-methyldihydromorphimethine methyl ether*, m. p. 127—128°, the *hydriodide* of which, decomposing at 155—156°, was also investigated. When boiled with acetic anhydride and sodium acetate, it formed 4-*acetoxy*-3:4-*dimethoxyphenanthrene*, m. p. 196°, the constitution of which follows from its conversion into 3:4:8-trimethoxyphenanthrene and its picrate. As by-product of the action of acetic anhydride, a *substance* was isolated, the *hydriodide*

of which had m. p. 190—195°, and decomposed at 215°. Analyses corresponded with the formula $C_{24}H_{29}O_6N,HI,2H_2O$. Concentrated potassium hydroxide liberated a *base*, which sintered at 78°, evolved gas at 105°, and was completely decomposed at about 125°. H. W.

Syntheses in the Pyrrole Group. V. α-, β-, and γ-Pyrryl Diketones. BERNARDO ODDO and CESARINA DAINOTTI (*Gazzetta*, 1912, 42, i, 716—726. Compare Oddo, Abstr., 1911, i, 496).—*Dipyrroylmethane*, $CH_2(CO\cdot C_4NH_4)_2$, is obtained by the action of magnesium pyrryl iodide (2 mols.) on malonyl chloride (1 mol.) in ether and decomposing with ice. The compound is extracted by means of boiling water and crystallised from benzene. It forms a *copper* and a *silver* salt.

Dipyrroylmethane reacts with phenylhydrazine acetate, yielding 1-*phenyl*-3 : 5-*dipyrrylpyrazolone*, $C_4NH_4\cdot C{<}{\genfrac{}{}{0pt}{}{N\cdot NPh}{CH}}{>}C\cdot C_4NH_4$, which separates from a mixture of benzene and light petroleum in pale yellow crystals, m. p. 166° (decomp.). It is reduced to the pyrazoline compound by sodium and alcohol.

*Dipyrryl*iso*oxazole*, $C_4NH_4\cdot C{<}{\genfrac{}{}{0pt}{}{N\cdot O}{CH}}{>}C\cdot C_4NH_4$, prepared by the action of hydroxylamine on dipyrroylmethane, forms yellow crystals, m. p. 167°. Concentrated potassium hydroxide converts dipyrroylmethane into pyrryl methyl ketone.

s-*Dipyrroylethane*, $C_2H_4(CO\cdot C_4NH_4)_2$, is prepared in similar manner from succinyl chloride, and forms pearly crystals, m. p. 234—235° (decomp.). The *dioxime*, $C_{12}H_{14}O_2N_4$, is a white powder, m. p. 175° (decomp.).

Dipyrroylmonoxime, $C_{10}H_9O_3N_3$, forms pale yellow crystals, m. p. 147°. C. H. D.

Syntheses in the Pyrrole Group. VI. Action of Organic Anhydrides on Magnesium Pyrryl Compounds. BERNARDO OTTO and CESARINA DAINOTTI (*Gazzetta*, 1912, 42, i, 727—730. Compare Oddo, Abstr., 1910, i, 426; 1911, i, 496).—It has been shown that acyl chlorides and magnesium pyrryl compounds yield ketones instead of tertiary carbinols. It is now found that acid anhydrides react in a similar manner, giving a still better yield. Thus magnesium pyrryl iodide and acetic anhydride form pyrryl methyl ketone, whilst benzoic anhydride yields phenyl pyrryl ketone.

C. H. D.

Some Derivatives of Triacetonamine. CHARLES HUGH CLARKE and FRANCIS FRANCIS (*Ber.*, 1912, 45, 2060—2065).—Triacetonalkamine (4-hydroxy-2 : 2 : 6 : 6-tetramethylpiperidine), obtained by reduction of triacetonamine (2 : 2 : 6 : 6-tetramethyl-4-piperidone, E. Fischer, Abstr., 1884, 1290), is converted by the action of benzoyl chloride and alkali into the *dibenzoyl* derivative, m. p. 200°; benzoylation in pyridine solution gives a quantitative yield of the *monobenzoate* (*O*-derivative), needles, m. p. 97—98°; *hydrochloride*, m. p. 240°; the physiological effect was examined with the easily soluble *lactate*, m. p.

100° (compare Vinci, Abstr., 1899, ii, 316). *Nitrosotriacetonalkamine*, obtained by the action of potassium nitrite on the sulphate of the base, forms pale yellow needles, m. p. 93°.

The action of magnesium ethyl iodide on an ethereal solution of anhydrous triacetonamine gives a poor yield of 4-*hydroxy*-2 : 2 : 6 : 6-*tetramethyl*-4-*ethylpiperidine*, m. p. 62°; *platinichloride*, m. p. 218°; the *hydriodide*, colourless prisms, m. p. 195°, when fused loses a molecule of water with the formation of the *hydriodide* of 4-*ethyltriacetonine* (2 : 2 : 6 : 6-*tetramethyl*-4-*ethyl*-1 : 2 : 5 : 6-*tetrahydropyridine*),

$$EtC\begin{cases}CH_2\cdot CMe_2\\CH-CMe_2\end{cases}NH,$$

a liquid of odour resembling piperidine; *hydriodide*, needles, m. p. above 270°; *nitrate*, m. p. 195° (decomp.).

4-Hydroxy-4-phenyl-2 : 2 : 6 : 6-tetramethylpiperidine, obtained in poor yield by the action of magnesium phenyl bromide on triacetonamine, has m. p. 130°.

Nitrosotriacetonamine (Heintz, this Journ., 1877, i, 592) when reduced by an acid alcoholic solution of stannous chloride gives *triacetonamineoxime*, m. p. 153°. In a similar manner the nitrosoamine of vinyldiacetonamine (nitroso-2 : 2 : 6-trimethyl-4-piperidone), m. p. 58°, is converted into vinyldiacetonamineoxime (4-oximino-2 : 2 : 6-trimethylpiperidine), m. p. 150°. Nitrosotriacetonalkamine, however, under similar treatment yields triacetonalkamine. It is probable that in the first two cases the nitroso-group is first reduced and then split off as hydroxylamine, which then reacts with the ketonic group. A suggestion is made that a substance obtained in small amount by Heintz from the treatment of nitrosotriacetonamine with acids may have been the above triacetonamineoxime.

D. F. T.

Equilibrium in Systems Consisting of Lead Halides and Pyridine. GEORGE W. HEISE (*J. Physical Chem.*, 1912, **16**, 373—381).—Various molecular compounds of pyridine with lead chloride, bromide, and iodide have been described from time to time, but the solubility curves have not been investigated. As a result of these measurements of the solubilities over a wide temperature range it is shown that none of the compounds previously mentioned exists, except the substance $PbBr_2,2C_5H_5N$, but on the other hand a number of new compounds are described.

The *substance*, $PbI_2,3C_5H_5N$, is stable below +6°, and forms an eutectic with solid pyridine at −43·5°. Between +6° and the boiling point of pyridine the *substance*, $PbI_2,2C_5H_5N$, is the stable form. Both of these substances separate in minute chalk-white crystals, which may be dried in the air and analysed very readily by volatilising the pyridine at 150°.

The solubility curve of lead bromide in pyridine has a well defined minimum at the transition point (+19°). From −26° to +19° the *substance*, $PbBr_2,3C_5H_5N$, with a negative temperature-coefficient of solubility, is the stable form. From +19° upwards, the substance $PbBr_2,2C_5H_5N$, previously described by Goebbels, separates.

These substances are both very unstable, losing pyridine rapidly in the air.

Lead chloride forms only one compound with pyridine between $-20°$ and $+110°$, namely, the *substance*, $PbCl_2,2C_5H_5N$; this separates in needles which lose pyridine rapidly in the air, and are, therefore, difficult to obtain in a suitable condition for analysis.

R. J. C.

Synthesis of 4-Phenyl-2-methylquinoline and 2 : 4-Diphenylquinoline. ROSARIO SPALLINO and G. SALIMEI (*Gazzetta*, 1912, **42**, i, 607—612).—A mixture of 2 parts of acetanilide, 1 part of acetophenone, and 2 parts of fused zinc chloride is heated in a sealed tube at 250—300° for four days, the product is extracted with chloroform, and the portion dissolved is recovered and distilled. The fraction passing over between 250° and 350°, yields an abundant precipitate with alcoholic picric acid, from which the base is obtained. 4-Phenyl-2-methylquinoline (compare Geigy and Konigs, Abstr., 1885, 1236) forms transparent tablets, m. p. 98—99°; the sulphate has m. p. 235°, and the hydrochloride, m. p. 219° (both decomp.); the picrate has m. p. 206—207°. The base condenses with chloral, and the resulting compound, $C_9NH_5Ph{\cdot}CH{:}CH{\cdot}CCl_3$, forms white needles, m. p. 198°.

If benzanilide is used in place of acetanilide, the product is 2 : 4-*diphenylquinoline*, $C_{11}H_{15}N$, forming white crystals, m. p. 106—107°. The *platinichloride* decomposes at 200° without melting; the picrate has m. p. 198°

C. H. D.

Action of Primary Amines on the Dinitrosoacyls (Glyoxime Peroxides or Diacylfuroxans). III. JACOB BÖESEKEN and D. P. ROSS VAN LENNEP (*Rec. trav. chim.*, 1912, **31**, 196—205).—The product of the action of any amine on dibenzoylglyoxime peroxide is an aminodioxime, which easily loses water and gives a coloured compound, for which three formulæ have been suggested:

$$\begin{array}{ccc} \begin{array}{l} NHR{\cdot}C{=\!=}N \\ COPh{\cdot}C{:}N{\cdot}O \end{array} & \begin{array}{l} NR{:}C{-\!-}NH \\ COPh{\cdot}C{:}N{\cdot}O \end{array} & \begin{array}{l} NHR{\cdot}C{:}N{\cdot}O \\ NO{\cdot}C{=\!=}CPh{\cdot} \end{array} \\ \text{(I.)} & \text{(II.)} & \text{(III.)} \end{array}$$

Formula III is put forward by Wieland and Gmelin (Abstr., 1909, i, 610), since they have succeeded in replacing an oxygen atom by two hydrogen atoms, so destroying the colour and giving a compound with the properties of a primary aromatic amine.

The authors have studied the original reaction with ammonia as the amine, and from their results they put forward three other formulæ:

$$\begin{array}{ccc} \begin{array}{l} NH_2{\cdot}C{=\!=}N \\ \quad O{\cdot}N{:}C{\cdot}COPh \end{array} & \begin{array}{l} NH{:}C{-\!-}NH \\ \quad O{\cdot}N{:}C{\cdot}COPh \end{array} & \begin{array}{l} HN{\cdot}N{:}C{\cdot}COPh \\ HO{\cdot}C{=\!=}N \end{array} \\ \text{(IV.)} & \text{(V.)} & \text{(VI.)} \end{array}$$

On adding dibenzoylglyoxime peroxide to an excess of ammonia, it dissolves to a deep yellow solution, from which, on warming, there separates a mass of crystals, which by repeated crystallisation can be separated into benzamide and 5-imino-3-benzoylfurazan (formula V), m. p. 135° (compare Holleman, Abstr., 1893, i, 205). This substance

is not acted on by thionyl chloride, but with phosphorus pentachloride it gives a dichloride, reconvertible by water into the original compound. It is destroyed by warming with alcoholic potassium hydroxide, does not form salts with acids, cannot be diazotised, and does not combine with potassium *iso*cyanate, all of which properties eliminate formulæ IV and VI.

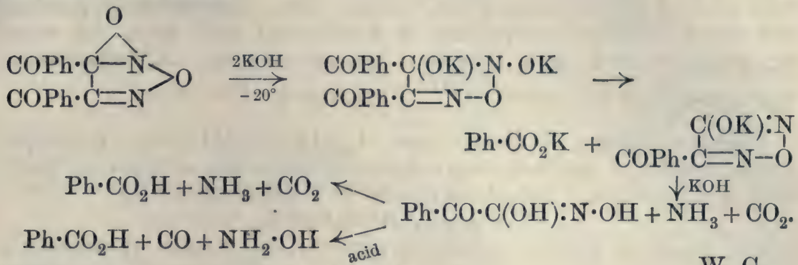
On agitating a suspension of iminobenzoylfurazan with alcoholic potassium hydroxide in the cold, it gives the *potassium* salt of 5-keto-3-benzoyl-ψ-furazan, $\begin{array}{l} O{:}C{-\!-}NH \\ \,\vert \quad\;\; \vert \\ O{\cdot}N{:}C{\cdot}COPh \end{array}$, giving a neutral aqueous solution, from which hydrochloric acid precipitates the *ketofurazan* as a white compound, which is decomposed by water on attempting crystallisation. Determination of its conductivity showed it to be a fairly strong acid ($K = 3{\cdot}3$). It yields a *silver* salt, soluble in ammonia, from which it separates in brilliant crystals, $C_6H_5CO{\cdot}C_2N_2O_2Ag + NH_3$. On heating the potassium salt with an excess of alkali, it yields potassium benzoate, cyanamide, and carbonate. W. G.

Configuration of the Dinitrosoacyls (Diacylglyoxime Peroxides). JACOB BÖESEKEN and M. C. BASTET (*Rec. trav. chim.*, 1912, 31, 206—220).—The authors have studied the behaviour of dibenzoylglyoxime peroxide towards phosphorus pentachloride and potassium hydroxide with the idea of elucidating the constitution of the compound. Difficulties arose in separating the products of the successive stages of the reaction with the second reagent.

On gradually adding the glyoxime peroxide to an excess of phosphorus pentachloride at 110°, a viscid oil is formed, which, on careful treatment with ice, gives 2 : 3-*dichloro*-3 : 4-*dibenzoylfurazan*, $\begin{array}{l} COPh{\cdot}CCl{-}NCl \\ \qquad\quad \vert \qquad \vert \\ COPh{\cdot}C{:}N{\cdot}O \end{array}$, white needles, m. p. 124—125°. It is stable towards boiling acetic acid and reducing agents in acid solution. With alkali hydroxides or ammonia, it is decomposed, giving benzoic acid and a hydroxamic acid.

Wieland and Semper (Abstr., 1908, i, 108) obtained by the action of sodium hydroxide on phenylglyoxime peroxide at 0° a compound, which they named hydroxyphenylfurazan, and to which they gave the constitution $\begin{array}{l} HO{\cdot}C{:}N{\cdot}O \\ \qquad \vert \qquad \vert \\ \qquad CPh{:}N \end{array}$, the triatomic ring of the glyoxime peroxide being opened. At this temperature, dibenzoylglyoxime peroxide, when similarly treated, is decomposed, giving benzoic and hydroxamic acids. Working in acetone solution at $-20°$, the authors have, however, been able to divide the decomposition into several stages. One molecule of potassium hydroxide is immediately neutralised, benzoic but not hydroxamic acid being formed. A similar result is obtained using two molecules of the alkali. On acidifying, glyoxime peroxide is regenerated. With more than two molecules of the alkali at $-20°$, or with less alkali at 0°, a hydroxamic acid is formed, and the pentatomic ring is opened, benzoic acid, ammonia, and carbon dioxide being generated in two stages. If, however, at the end of the first stage the liquid is boiled with phosphoric or hydrochloric acids, the nitrogen is

then eliminated as hydroxylamine. The complete course of the reaction is as follows:



W. G.

Leuco-bases and Dyes Derived from Diphenylethylene; Preparation of Two *cyclo*Hexylidene Bases. Paul Lemoult (*Compt. rend*, 1912, **155**, 217—219).—Schmidlin and Escher (this vol., i, 437) having questioned the author's preparation of tetramethyldiaminodiphenyl*cyclo*hexylidenemethane from Michler's ketone and magnesium *cyclo*hexyl bromide (Abstr., 1911, i, 399) on account of lack of detail, a full detailed account of the preparation is now given, and the author claims that it is an improvement on their method, since he reduces the time of heating from sixty to six hours, and obtains a yield of 82%. The corresponding *tetraethyl* compound can be similarly prepared, and is obtained in pale yellow prisms, m. p. 74°.

W. G.

Dehydroindigotin. IV. Additive Compounds. Ludwig Kalb (*Ber.*, 1912, **45**, 2136—2149).—5 : 7 : 5′ : 7′-*Tetrabromodehydroindigotin* 2 : 2′-*diacetate*,

$$C_6H_2Br_2{<}^{NH}_{CO}{>}C(OAc)\cdot C(OAc){<}^{NH}_{CO}{>}C_6H_2Br_2,$$

yellow prisms or leaflets, is obtained by heating a finely divided suspension of 5 : 7 : 5′ : 7′-tetrabromoindigotin in glacial acetic acid with powdered potassium permanganate on the water-bath. The substance does not dissociate in boiling chloroform or benzene, but when heated in carbon tetrachloride and a little pyridine is converted into 5 : 7 : 5′ : 7′-*tetrabromodehydroindigotin*,

$$C_6H_2Br_2{<}^{-N}_{CO}{\gg}C\cdot C{\ll}^{N-}_{CO}{>}C_6H_2Br_2.$$

This substance forms violet-brown crystals with a copper lustre, is decomposed by boiling pyridine, develops a blue coloration with sulphuric acid, and is stable in boiling water and concentrated hydrochloric acid. Tetrabromodehydroindigotin is converted into the following derivatives by warming with benzene and the requisite acid; *tetrabromodehydroindigotin dihydrochloride*,

$$C_{16}H_4O_2N_2Br_4,2HCl,$$

yellowish-green, crystalline powder; *diformate*,

$$C_{16}H_4O_2N_2Br_4,2H_2CO_2,$$

yellowish-green, crystalline powder; *dibenzoate*,

$$C_{16}H_4O_2N_2Br_4,2Ph\cdot CO_2H,$$

yellowish-green leaflets.

Reasons are given for regarding the preceding additive compounds, except the dihydrochloride, as *CC'*-derivatives (formulæ correspond with that of the diacetate given above). The dihydrochloride, unlike the other additive compounds, is decomposed very easily by water or pyridine, and may therefore be possibly an *NN'*-derivative, $C_6H_2Br_2<\begin{smallmatrix}N(HCl)\\CO\end{smallmatrix}>C{\cdot}C<\begin{smallmatrix}N(HCl)\\CO\end{smallmatrix}>C_6H_2Br_2$.

Dehydroindigotin 2 : 2'-*diformate*, $C_{16}H_8O_2N_2,2\frac{1}{2}H_2CO_2$, yellowish-green needles, is obtained from dehydroindigotin and anhydrous formic acid in chloroform. *Dehydroindigotin* 2 : 2'-*dihydrocyanide*,

$$C_{16}H_8O_2N_2,2HCN,C_5NH_5,$$

green, quadratic plates containing pyridine, is obtained by shaking a suspension of dehydroindigotin in cold pyridine with anhydrous hydrogen cyanide. The substance, from which the pyridine cannot be removed without decomposition, is dissociated by boiling alcohol or toluene, and is reduced to indigo-white by alkaline sodium hyposulphite. *Dehydroindigotin* 2 : 2'-*diphenolate*, $C_{16}H_8O_2N_2,2PhOH$, yellow needles, and *dehydroindigotin phenolate*, $C_{16}H_8O_2N_2,PhOH$, are obtained by shaking dehydroindigotin with a well-cooled mixture of chloroform, phenol, and pyridine; the two additive compounds are separated by acetone, in which the phenolate is easily soluble. The constitution of the phenolate is unknown; the substance has not been converted into a derivative of indigotin or of dehydroindigotin. C. S.

2-Phenylindolone and Phenylindoxyl. LUDWIG KALB and JOSEPH BAYER (*Ber.*, 1912, **45**, 2150—2162).—The abnormal reactions of the azomethine group in dehydroindigotin and the uncertainty of the constitution of its dihydrochloride (preceding abstract) led the authors to examine the behaviour of similarly constituted, but less complex, compounds.

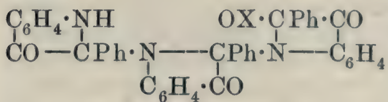
3-Amino-2-phenylindole, which is best obtained by the reduction of 3-oximino-2-phenylindole by alkaline sodium hyposulphite, is suspended in benzene, and the hot mixture is treated with lead peroxide. The resulting 3-*imino*-2-*phenylindole*, $C_6H_4<\begin{smallmatrix}N\\C(:NH)\end{smallmatrix}>CPh$, m. p. 114·5°, glistening, orange-yellow leaflets, is hydrolysed by ethereal oxalic acid to 2-*phenylindolone*, $C_6H_4<\begin{smallmatrix}N\\CO\end{smallmatrix}>CPh$, dark red crystals, m. p. 102°, and is converted by concentrated hydrochloric acid into 2-*phenylindolone* N-*hydrochloride*, $C_6H_4<\begin{smallmatrix}N(HCl)\\CO\end{smallmatrix}>CPh$, reddish-brown needles, which is converted into 2-phenylindolone very conveniently by boiling benzene and a little calcium oxide.

Whilst resembling dehydroindigotin in its property of forming abnormal additive compounds, 2-phenylindolone also exhibits distinctly basic properties, and forms true salts with mineral acids. The additive compounds are pale yellow, and in their behaviour correspond with the similar derivatives of dehydroindigotin. The *methyl alcoholate*, $C_6H_4<\begin{smallmatrix}NH\\CO\end{smallmatrix}>CPh{\cdot}OMe$, quadratic leaflets, and the analogously constituted additive *compounds* with ammonia, m. p.

168°, with aniline, m. p. about 134°, and with potassium hydrogen sulphite are described. The *acetate*, $3C_{14}H_9ON,CH_3\cdot CO_2H$, m. p. 168°, *propionate*, $3C_{14}H_9ON,CH_2Me\cdot CO_2H$, m. p. 204°, and *hydrate*,

$$3C_{14}H_9ON,H_2O,$$

m. p. 168°, are stable to boiling water or toluene, are dissociated by boiling acetic acid, benzaldehyde, or nitrobenzene, and receive the annexed formula (in which X is H, OAc, or $O\cdot CO\cdot CH_2Me$), which are similar to those of the simple additive compounds. The additive compounds of 2-phenylindolone with formic, trichloroacetic, hydrochloric, sulphuric, and other strong acids are deeply coloured, and are easily dissociated in indifferent solvents or by water or alcohol. These phenomena of dissociation and of halochromy indicate, therefore, that the additive compounds of 2-phenylindolone with strong acids are true salts; consequently they receive constitutions similar to that of the hydrochloride given above. The fact that the dihydrochloride of dehydroindigotin does not exhibit halochromy is strong evidence of its constitution as a CC′-derivative (preceding abstract).



By reduction with hydrochloric acid and stannous chloride, 2-phenylindolone hydrochloride yields 2-*phenylindoxyl*, $C_6H_4<\genfrac{}{}{0pt}{}{NH}{C(OH)}>CPh$, which partly melts and decomposes at 140—145°, and is obtained in colourless leaflets by crystallisation from dry boiling carbon tetrachloride in an atmosphere of carbon dioxide; the compound is quite different from the various substances described as 2-phenylindoxyl in the literature.

When 2-phenylindoxyl is dissolved in boiling benzene, autoxidation occurs, and 2-phenylindolone is produced. The two substances react to form an additive *compound*, m. p. 180—181°, reddening at 178°, yellow needles, which probably has the constitution:

$$C_6H_4<\genfrac{}{}{0pt}{}{NH}{CO}>CPh\cdot O\cdot C\leqslant\genfrac{}{}{0pt}{}{CPh}{C_6H_4}>NH.$$

It is also obtained as an intermediate product in the reduction of 2-phenylindolone or the oxidation of 2-phenylindoxyl.

When 2-phenylindolone or 3-imino-2-phenylindole is boiled with dilute sodium hydroxide and a little alcohol, the solution yields 3-phenyldioxindole by acidification. Migration of the phenyl group from position 2 to 3 must have occurred. C. S.

N-Methyl Derivatives of Indigotin. LEO ETTINGER and PAUL FRIEDLÄNDER (*Ber.*, 1912, 45, 2074—2080. Compare A. von Baeyer, Abstr., 1884, i, 76).—3-Acetyl-1-methylindoxyl (compare Vorländer and Mumme, Abstr., 1902, i, 451, 454), tablets, m. p. 57°, is obtained by boiling methylanthranilic acid with excess of chloroacetic acid in alkaline solution, and heating the product with a mixture of acetic anhydride and anhydrous sodium acetate. When it is dissolved in dilute alcohol to which ammonia has been added, and oxidised by a current of air, 1 : 1′-*dimethylindigotin*, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NMe}>C:C<\genfrac{}{}{0pt}{}{CO}{NMe}>C_6H_4$, separ-

ates in needles with a coppery lustre. The same dimethylindigotin is also obtained by the reduction of 1-methylisatin-2-anil,

$$C_6H_4<\begin{matrix}CO\\NMe\end{matrix}>C:NPh$$

(Pummerer, Abstr., 1911, i, 231), in aqueous alcohol containing a little ammonia by hydrogen sulphide. It forms needles, m. p. 182°, and sublimes at a higher temperature; it is generally much more soluble than indigotin, and the benzene solution possesses a colour resembling that of malachite-green; alkaline hyposulphite reduces it to a pale yellow vat (which is only slightly absorbed by the fibre), from which on the addition of an alkali hydrogen carbonate, the *leuco*-compound separates in pale yellow needles. Dimethylindigotin is more strongly basic than indigo, and can be completely extracted from its benzene solution by hydrochloric acid, D 1·19.

1-*Methylindigotin* can be obtained by atmospheric oxidation of a mixture of indoxyl and 1-methylindoxyl in ammoniacal solution, and also by warming in acetic acid solution a mixture of indoxyl, 1-methylisatin-2-anil, and acetic anhydride; in the latter preparation a considerable quantity of another *substance*, crystallising in brownish-red needles, is obtained. In either method of preparation the methylindigotin is best isolated by extraction with sulphuric or hydrochloric acid and reprecipitating by the addition of water; it forms coppery needles (from benzene), which, on heating, sublime with partial decomposition; the colour of its solutions approaches more closely that of the above dimethylindigotin than that of indigotin, the maximum absorption in xylene solution for dimethylindigotin, methylindigotin, and indigotin occurring at λ 644·5, λ 639·4, and λ 590·9 respectively.

5-*Chloroisatin*-p-*chloroanil* can be obtained by Sandmeyer's method from *p*-chloroaniline; it forms violet-black needles, m. p. 205—206°, and by treatment with methyl sulphate and sodium ethoxide gives 5-*chloro*-1-*methylisatin*-p-*chloroanil*, brownish-red needles, m. p. 165—166°; this can be converted into 5 : 5′-*dichloro*-1 : 1′-*dimethylindigotin*, $C_6H_3Cl<\begin{matrix}CO\\NMe\end{matrix}>C:C<\begin{matrix}CO\\NMe\end{matrix}>C_6H_3Cl$, needles, which are insoluble in aqueous hydrochloric acid. The solutions in benzene hydrocarbons show maximum absorption at λ 665.

In a similar manner, *p*-toluidine can be converted into 1 : 5-*dimethylisatin*-p-*toluidide*, red needles (from alcohol), m. p. 185—186°, which can be further converted into 1 : 1′ : 5 : 5′-*tetramethylindigotin*, $C_6H_3Me<\begin{matrix}CO\\NMe\end{matrix}>C:C<\begin{matrix}CO\\NMe\end{matrix}>C_6H_3Me$, deep blue needles, giving solutions of maximum absorption at λ 665.

For the preparation of 6 : 6′-dibromo-1 : 1′-dimethylindigotin, 2-nitro-4-aminobenzoic acid by diazotisation and the Sandmeyer reaction was converted into 4-bromo-2-nitrobenzoic acid, which by reduction gave 4-bromoanthranilic acid; this was methylated by the action of methyl sulphate on its solution in aqueous sodium carbonate, and the product purified by conversion into 4-bromo-2-nitrosoaminomethylbenzoic acid, needles, m. p. 160°, by reduction of which the

pure 4-*bromo-2-methylaminobenzoic acid*, $NHMe\cdot C_6H_3Br\cdot CO_2H$, needles, m. p. 189°, was obtained. From this, the action of chloroacetic acid in the usual way gave 2-*bromo-6-carboxyphenylmethylaminoacetic acid*, $CO_2H\cdot C_6H_3Br\cdot NMe\cdot CH_2\cdot CO_2H$, prisms, m. p. 188°, which by boiling with acetic anhydride and sodium acetate was converted into 6-*bromo-3-acetyl-1-methylindoxyl*, $C_6H_3Br<\substack{COAc\\NMe}>CH$, grey needles, m. p. 95°; this was cautiously hydrolysed to 6-bromo-1-methylindoxyl, and the action of potassium ferricyanide on an alkaline solution of this produced 6:6′-*dibromo*-1:1′-*dimethylindigotin*, coppery needles, which gave a solution in xylene showing maximum absorption at λ 638, whereas maximum absorption by 6:6′-dibromoindigotin is at λ 587·5.

The substitution of methyl groups into the imino-groups of indigotin is therefore of greater influence on the colour than is substitution in the benzene rings. D. F. T.

6:6′-Dibromoindirubin. LEO ETTINGER and PAUL FRIEDLÄNDER (*Ber.*, 1912, **45**, 2081—2083).—The 6:6′-dibromoindigotin obtained from *Murex brandaris* (Friedländer, Abstr., 1909, i, 262) is not accompanied by 6:6′-dibromoindirubin.

6:6′-Dibromoindirubin can be synthesised from 6-bromoisatin and 6-bromoindoxyl; the latter is already known, whilst the necessary 6-bromoisatin can be obtained by Sandmeyer's method.

m-Bromoaniline can be converted through the thiocarbamide derivative into bromoisatinbromoanil, $C_6H_3Br<\substack{CO-\\NH}>C:N\cdot C_6H_4Br$; the product, violet-brown needles, m. p. 205—206°, proves to be a mixture of 6-*bromoisatin*-2-m-*bromoanil* with the isomeric 4-*bromo*-compound. The mixture when warmed with diluted sulphuric acid dissolves, and then a crystalline deposit of a mixture of two isomeric bromoisatins forms; this can be separated by alcohol into 6-*bromoisatin*, needles, m. p. 263—264° (decomp.), and 4-*bromoisatin*, tablets, m. p. 258—259° (uncorr.); the identity of these is proved by converting each into the corresponding dibromoindigotin, as all the symmetrical dibromoindigotins have been described.

If equivalent amounts of 6-bromoisatin and 6-bromoacetylindoxyl are warmed in glacial acetic acid solution with a little fuming hydrochloric acid, 6:6′-*dibromoindirubin* is obtained as a deposit of brown needles. It is sparingly soluble in most solvents, but easily in quinoline; alkaline hyposulphite reduces it to a yellow vat, which dyes cotton cherry-red. The xylene solution shows two absorption bands with maxima at λ 567μμ and λ 520μμ. D. F. T.

Constitution of the Cyanine Dyes. WALTER KÖNIG (*J. pr. Chem.*, 1912, [ii], **86**, 166—174. Compare Abstr., 1906, i, 207; Kaufmann, Abstr., 1911, i, 328).—The author discusses the various formulæ which have been assigned to the cyanine dyes, and shows that the properties and behaviour of these substances are most

satisfactorily represented by Kaufmann's formulæ, the cyanines having the constitution I and the *iso*cyanines formula II:

$$\text{(I.)}\ CH\Big<\begin{matrix}CH\text{——}CH\\ CH\cdot C(NHR)\end{matrix}\Big>C\cdot CH{:}CH\cdot CH{:}CH\cdot C\Big<\begin{matrix}C_6H_4\cdot NRI\\ CH\text{—}CH\end{matrix}.$$

$$\text{(II.)}\ CH\Big<\begin{matrix}CH\text{——}CH\\ CH\cdot C(NHR)\end{matrix}\Big>C\cdot CH{:}CH\cdot CH{:}CH\cdot C\Big<\begin{matrix}CH{=}CH\\ NRI\cdot C_6H_4\end{matrix}.$$

The formulæ explain the analogies existing between the pyridine and cyanine dyes, and also the formation of yellowish-white nitrosoamines by treating both the cyanines and *iso*cyanines with nitrous acid.

Further support is given to these formulæ by the synthesis of *dyes* (formula III and IV) resembling the cyanines by the condensation of 2- and 4-methylquinoline salts with *p*-dimethylaminobenzaldehyde in the presence of piperidine.

$$\text{(III.)}\ NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot C\Big<\begin{matrix}CH{=}CH\\ NMeX\cdot C_6H_4\end{matrix}.$$

$$\text{(IV.)}\ NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot C\Big<\begin{matrix}C_6H_4\cdot NMeX\\ CH\text{—}CH\end{matrix}.$$

These dyes are bluish-red to violet in colour, and show the characteristic behaviour of the cyanines of being almost completely decolorised by dilute acids.

It is also mentioned that salts of β-hydroxyacraldehydedianilide condense with 2- and 4-methylquinoline salts in the presence of piperidine, yielding dyes (formulæ V and VI) which exhibit in their chemical behaviour a great similarity to the *iso*cyanines, whilst the

$$\text{(V.)}\ NHR\cdot CH{:}CH\cdot CH{:}CH\cdot C\Big<\begin{matrix}CH{=}CH\\ NRX\cdot C_6H_4\end{matrix}$$

$$\text{(VI.)}\ NHR\cdot CH{:}CH\cdot CH{:}CH\cdot C\Big<\begin{matrix}C_6H_4\cdot NRX\\ CH\text{—}CH\end{matrix}.$$

condensation of aldehydes of the type $NRR'\cdot CH{:}CH\cdot CH{:}CH\cdot CHO$ (where $R =$ aryl and $R' =$ alkyl) with salts of 2- and 4-methylquinoline results in the formation of dyes (VII and VIII) resembling the cyanines.

$$\text{(VII.)}\ NRR'\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot C\Big<\begin{matrix}CH{=}CH\\ NR''I\cdot C_6H_4\end{matrix}.$$

$$\text{(VIII.)}\ NRR'\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot C\Big<\begin{matrix}C_6H_4\cdot NR''I\\ CH\text{—}CH\end{matrix}.$$

F. B.

Electrochemical Reductions. II. Reduction of Secondary Nitroamines to Hydrazines. H. J. Backer (*Rec. trav. chim.*, 1912, 31, 142—195. Compare this vol., i, 339).—Up to the present secondary nitroamines have only been reduced by zinc and acetic acid, the yield of the corresponding hydrazines being in all cases very poor. Alkyl nitroamides have not, as yet, been reduced to hydrazines. The author has reduced a number of secondary nitroamines and one alkylnitroamide by electrochemical methods, and has, in general, obtained much better yields. The best results were produced by employing a cathode of copper, coated with tin, and dilute sulphuric acid as the

electrolyte. To promote solution it was sometimes necessary to add acetic acid. The hydrazines, etc., were identified by preparation of hydrazones or analogous compounds with a number of aromatic aldehydes, or by interaction with cyanates, giving semicarbazides. The yield of hydrazine was determined either by titration in alkaline solution with mercuric chloride solution, or by weighing the tetrazone formed in this reaction.

Dimethylnitroamine is best reduced by using the copper cathode and 10% sulphuric acid as electrolyte. After reduction the solution is evaporated with hydrochloric acid, made alkaline with potassium hydroxide, and fractionated over barium oxide. *as*-Dimethylhydrazine gives an oxalyl derivative (compare Renouf, Abstr., 1881, 151) and a *picryl* derivative, m. p. 136·5°. *N*-Nitropiperidine gives a better yield of *N*-aminopiperidine by reduction with zinc and acetic acid than by electrochemical methods, using a nickel cathode and a 10% solution of sodium acetate as electrolyte.

For dinitropiperazine the best electrolyte is 50% acetic acid. The author has condensed the resulting diaminopiperazine with a number of aldehydes. The derivatives so obtained are all colourless, and are decomposed on warming with dilute sulphuric acid. Salicylaldehyde gives 1 : 4-*disalicylideneaminopiperazine*, $C_4N_2H_8(N{:}CH{\cdot}C_6H_4{\cdot}OH)_2$, white needles, m. p. 226°, which retains its phenolic character. With *o*-methoxybenzaldehyde there is produced 1 : 4-*di*-o-*methoxybenzylideneaminopiperazine*, $C_4N_2H_8(N{:}CH{\cdot}C_6H_4{\cdot}OMe)_2$, m. p. 207°. The corresponding derivative from anisaldehyde has m. p. 246·5°. Diaminopiperazine and potassium *iso*cyanate when mixed in aqueous solution give 1 : 4-*dicarbamidopiperazine*, $C_4N_2H_8(NH{\cdot}CO{\cdot}NH_2)_2$, colourless crystals, m. p. 286°, which in hydrochloric acid solution reacts with sodium nitrite, giving a *dinitroso*-compound, which is very unstable and decomposes at 74°, or on exposure to light or moisture. It is decomposed by alkalis, giving nitrous oxide, carbon dioxide, ammonia, and piperazine.

Ethylenebismethylnitroamine, as prepared by Franchimont and Klobbie (Abstr., 1889, 492) from ethylenediurethane by nitration, treatment with ammonia, and subsequent methylation, using, however, methyl sulphate instead of the iodide is best reduced by suspension in dilute acetic acid containing sodium acetate, the copper cathode being employed. The resulting hydrazine condenses with anisaldehyde, giving a *dianisylidenedimethylethylenedihydrazine*,

$$C_2H_4(NMe{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OMe)_2,$$

long, white needles, m. p. 147·5°. With *p*-nitrobenzaldehyde, *di*-p-*nitrobenzylidenedimethylethylenedihydrazine*, orange-red needles, m. p. 192·5°, is obtained, which on the addition of concentrated hydrochloric acid is converted into a pale yellow *compound*, $C_{18}H_{20}O_4N_6,2HCl$.

Phenylmethylnitroamine, which with concentrated nitric acid gives trinitrophenylmethylnitroamine (compare Franchimont, Abstr., 1910, i, 616), is electrically reduced in dilute acetic acid solution containing sodium acetate, giving *as*-phenylmethylhydrazine. On mixing this with *p*-nitrobenzaldehyde in alcoholic solution, the liquid is turned red, and deposits *phenyl*-p-*nitrobenzylidenemethylhydrazine*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NMePh,$$

as small, red needles, m. p. 135°. This red modification on trituration with petroleum or ether passes readily into a yellow modification, which has m. p. 130·5—131°. These two enantiotropic modifications are mutually transformable at different temperatures, the red being the more stable at higher temperatures. Phenylmethylhydrazine condenses with cinnamaldehyde to form *cinnamaldehyde-as-phenylmethylhydrazone*, m. p. 112·3°, and with phenyl *iso*cyanate it gives *diphenylmethylsemicarbazide*, NHPh·CO·NH·NMePh, white needles, m. p. 158·5°.

Methyl methylnitroaminoformate is best reduced in dilute sulphuric acid solution, and yields methyl methylhydrazinoformate, which is identified by boiling its solution with sodium hydroxide for several hours, when it is decomposed into methylhydrazine, methyl alcohol, and carbon dioxide. On oxidation by bromine water the hydrazine gives a tetrazone, m. p. 187·5° (compare Klobbie, Abstr., 1891, 292). With benzaldehyde it gives a *hydrazone*, m. p. 77·5°, and with *o*-nitrobenzaldehyde a *hydrazone*, m. p. 105·5°. W. G.

Reduction of the Ketonehydrazines and Ketazines of Tetramethyldi-*p*-aminobenzophenone and Fluorenone. THEODOR CURTIUS and KARL KOF (*J. pr. Chem.*, 1912, [ii], 86, 113—132).—Tetramethyldi-*p*-aminobenzophenonehydrazone (Wieland and Roseeu, Abstr., 1911, i, 571) is readily hydrolysed by cold concentrated sulphuric acid into its components, and on treatment with bromine vapour in acid solution yields successively brownish-red and dark green *dyes*. Towards iodine in alcoholic solution the hydrazone behaves similarly, the final product consisting of a dark blue, crystalline *substance*, of a metallic lustre, m. p. 240°, with previous softening at 209°.

Bistetramethyldi-p-*aminobenzophenonethiocarbohydrazide*,

$$CS[NH\cdot N{:}C(C_6H_4\cdot NMe_2)_2]_2,$$

prepared by heating the hydrazone for six hours with carbon disulphide in benzene solution, crystallises in citron-yellow needles, m. p. 233°; if the period of heating is shortened, a cinnabar-red, microcrystalline *substance*, having m. p. 222°, is produced.

When reduced with sodium amalgam and alcohol, or with aluminium amalgam in moist ethereal solution, tetramethyldi-*p*-aminobenzophenonehydrazone yields s-*ditetramethyldi*-p-*aminobenzhydrylhydrazine*, $N_2H_2[CH(C_6H_4\cdot NMe_2)_2]_2$, which forms small, white crystals, m. p. 285° (decomp.), dissolves in glacial acetic acid, yielding a blue coloration, probably due to the formation of the compound

$$\begin{matrix}NHMe_2\\|\\C_6H_4\end{matrix}\!\!>\!C(C_6H_4\cdot NMe_2)\cdot NH\cdot NH\cdot C(C_6H_4\cdot NMe_2)\!<\!\!\begin{matrix}NHMe_2\\|\\C_6H_4\end{matrix},$$

and on treatment with sodium nitrite and acetic acid, yields an orange *nitrosoamine* (?) melting indefinitely about 180°.

Benzaldehydetetramethyldi-p-*aminobenzhydrylhydrazone*,

$$CHPh{:}N\cdot NH\cdot CH(C_6H_4\cdot NMe_2)_2,$$

prepared by reducing tetramethyldi-*p*-aminobenzophenonebenzylidenehydrazone, $CHPh{:}N\cdot N{:}C(C_6H_4\cdot NMe_2)_2$ (Wieland and Roseeu, *loc. cit.*), with sodium amalgam and alcohol, crystallises in lustrous, colourless

needles, m. p. 143°, and dissolves in glacial acetic acid, yielding blue solutions which probably contain the compound

$$\begin{matrix} NHMe_2 \\ | \\ C_6H_4 \end{matrix} \!\! > C < \begin{matrix} NH\cdot N\colon CHPh \\ C_6H_4\cdot NMe_2 \end{matrix} .$$

It is hydrolysed by cold dilute hydrochloric acid to benzaldehyde and the above mentioned *s*-ditetramethyldi-*p*-aminobenzhydrylhydrazine.

When heated with zinc and dilute acetic acid, tetramethyldi-*p*-aminobenzophenonehydrazone is hydrolysed to Michler's ketone, which then undergoes further reduction to tetramethyldi-*p*-aminodiphenylmethane.

The azine of Michler's ketone is obtained by heating the ketone with either hydrazine hydrate or tetramethyldi-*p*-aminobenzophenonehydrazone and alcohol at 170° (compare Wieland and Roseeu, *loc. cit.*).

Oxidation of fluoronehydrazone with mercuric oxide in benzene solution gives rise to diphenyleneazomethylene (Staudinger and Kupfer, Abstr., 1911, i, 751), together with an amorphous, brick-red *substance*, m. p. 243°.

Fluorenonebenzylidenehydrazone crystallises in short, orange-red needles, m. p. 91—94°; Staudinger and Kupfer give 82—84°.

When reduced with sodium amalgam and alcohol, fluorenonehydrazone is converted into *di-9-fluorylamine*,

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} \!\! > CH\cdot NH\cdot CH < \!\! \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} ,$$

which crystallises in short, yellow needles, and melts at 167° to a green liquid.

The azine of fluorenone is obtained in violet-red crystals, m. p. 265°, by heating fluorenone with hydrazine hydrate or fluorenonehydrazone (compare Wieland and Roseeu, *loc. cit.*). On reduction with zinc dust and acetic acid it yields 9-acetylaminofluorene.

The compound described by Sorge (Abstr., 1902, i, 379) as *p*-tolyl methyl ketonehydrazone is found by the authors to consist of p-*tolylmethylketazine*, $N_2(\colon CMe\cdot C_6H_4Me)_2$, which has m. p. 136°, and is best obtained by heating the ketone with hydrazine hydrate and alcohol at 140°. All attempts to prepare the hydrazone proved unsuccessful.

F. B.

Unusual Oxidation of an Azo-compound. EUGEN BAMBERGER and OSCAR BAUDISCH (*Ber.*, 1912, 45, 2054—2059. Compare Abstr., 1909, i, 977).—The oxidation of *syn*-*p*-chlorodiazobenzene cyanide in ethereal solution with hydrogen peroxide in the presence of magnesium carbonate follows an unusual course. The ethereal liquid when extracted with barium hydroxide solution gives a precipitate (leaflets) of the barium salt of *p*-chloronitrosophenylhydroxylamine, which on treatment with cold hydrochloric acid yields the free *p*-chloronitrosophenylhydroxylamine, $C_6H_4Cl\cdot N(NO)\cdot OH$ (m. p. 73·5—74·5°). The residual ethereal solution on evaporation leaves orange-red crystals of *p*-chlorophenylazoformamide,

$$C_6H_4Cl\cdot N\colon N\cdot CO\cdot NH_2,$$

m. p. 181—182° (compare Hantzsch and Schultze, Abstr., 1895, i, 658).

On oxidation in a similar manner, but in the presence of sodium hydroxide solution in place of magnesium carbonate, *syn-p*-chlorodiazobenzene cyanide gives *p*-chlorophenylazoformamide with a very small quantity of nitrosophenylhydroxylamine.

iso-(anti-)p-Chlorodiazobenzene cyanide when treated as above with hydrogen peroxide in the presence of magnesium carbonate is chemically unaffected.

The first-named of the authors in a footnote states that he now accepts the analogy between the steric behaviour of the diazo-compounds and the oximes; he points out the similarity of the oxidation of the normal (*syn*-)diazotates to a benzenediazoic acid and a nitrosophenylhydroxylamine (Bamberger and Baudisch, *loc. cit.*):

$$\underset{\ddot{\mathrm{O}}}{\mathrm{NPh{:}NONa}} \leftarrow \mathrm{NPh{:}NONa} \rightarrow \underset{\ddot{\mathrm{O}}}{\mathrm{NPh{:}NONa}},$$

with the oxidation of the oximes to a hydroxamic acid and a substituted nitromethane (Bamberger, Abstr., 1900, i, 500),

$$\underset{\dot{\mathrm{O}}\mathrm{H}}{\mathrm{CPh{:}N{\cdot}OH}} \leftarrow \mathrm{CHPh{:}N{\cdot}OH} \rightarrow \underset{\ddot{\mathrm{O}}}{\mathrm{CHPh{:}N{\cdot}OH}}\ (\rightarrow \mathrm{CH_2Ph{\cdot}NO_2}).$$

D. F. T.

Heat Coagulation of Proteins. III. The Influence of Alkali on Reaction Velocity. Harriette Chick and Charles J. Martin (*J. Physiol.*, 1912, **45**, 61—69. Compare Abstr., 1911, i, 822).—The denaturation rate of egg-albumin in alkaline solutions is increased by increased concentration of hydroxyl ions, just as it is by hydrogen ions in acid solution. As denaturation proceeds, hydroxyl ions are continuously removed, but if the alkalinity is kept constant by the presence of excess of solid magnesium oxide, denaturation proceeds as a reaction of the first order, as was also shown in the case of acid.

The influence of acids and alkalis on this phenomenon is compared with their effect on the viscosity and precipitability by alcohol of protein solutions, and on the imbibition of water by protein. It is suggested that protein in the form of salts is in more intimate association with water. W. D. H.

The Precipitation of Suspensoid Protein by Various Ions. W. Nevill Heard (*J. Physiol.*, 1912, **45**, 27—38).—The power of an electrolyte to precipitate negatively-charged suspensoid protein is primarily dependent on the valency of the cation, but this is greatly modified by the relation of the latter to the OH-group and its capacity to reduce the ionisation of that group.

Positively charged suspensoid protein being kept in solution by the charge given it by the H ion, the power of the anion to precipitate is due to its capacity to reduce the ionisation of the compound of acid and protein. Although the cation is the principal element in the precipitation of alkaline protein, and the anion in the precipitation of acid protein, the accompanying ion is probably never without some effect.

W. D. H.

The Conditions for the Complete Hydrolysis of Proteins. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1912, **12**, 295—300).—The percentage of amino-nitrogen reaches a definite maximum when acid hydrolysis of a protein is complete, and this maximum is the same whether the hydrolysis occurs at 100° or 150°. The ammonia does not reach a definite maximum, but increases the longer the hydrolysis continues. W. D. H.

Complex Compounds of Ferrous Salts, Hydrogen Peroxide, and Proteins; On the Part Played by Iron in Biological Oxidation Processes. FRANZ RÖHMANN and T. SHMAMINE (*Biochem. Zeitsch.*, 1912, **42**, 235—249).—Iron by itself, in colloidal or protein solutions, is not capable of causing oxidation by molecular oxygen to the extent at which oxidative processes take place in the organism. Dyad- or triad-iron (the latter probably only after preliminary reduction) forms compounds with hydrogen peroxide which have a strong oxidative capacity. In solutions of certain proteins (egg-white, sodium nucleate, and proteoses from Witte's peptone), ferrous salts can remain in solution, which in conjunction with hydrogen peroxide can bring about energetic oxidation. If suitable proportions of protein, iron salts, and hydrogen peroxide be chosen, precipitates can be produced, several of which are described by the authors under the name of oxyferrous-protein compounds. Such substances have the property of blueing guaiacum tincture, and in the presence of excess of hydrogen peroxide, oxidising substances like pyrogallol and quinol. They can thus act as oxygenases or peroxydases. It is suggested that similar compounds can play an active part in the oxidative processes in the cell. S. B. S.

Compounds of Ferric Salts with Albumoses. FRANZ RÖHMANN and T. SHMAMINE (*Biochem. Zeitsch.*, 1912, **42**, 250—254).—On addition of simple ferric salts, such as the sulphate to a solution of Witte's peptone, a precipitate containing both iron and sulphate is obtained. The substance has the properties of an acid insoluble in water, as it dissolves in alkalis giving a solution which is neutral to turmeric paper. If such a solution is treated with excess of alkali, the iron is precipitated as hydroxide. If barium hydroxide is used, barium compounds of albumose pass into solution. On treatment of the solution with the theoretical quantity of sulphuric acid necessary to combine with the barium, a part of the albumoses is separated with the barium sulphate as a substance insoluble in water, which is, however, soluble both in acids and alkalis. It is suggested that these reactions might be employed for separating certain constituents from digestion mixtures. S. B. S.

Fibrinogen. I. The Biological Differentiation of the Three Proteins of Blood Plasma. JULIUS BAUER and ST. ENGEL (*Biochem. Zeitsch.*, 1912, 42, 399—402).—Just as caseinogen can be differentiated from lactoglobulin and lactalbumin (which according to the authors are identical with serum-globulin and serum-albumin), so

fibrinogen can be differentiated from the other blood proteins. The methods of differentiation employed were those of the precipitation reaction and the deviation of the complement. The fibrinogens from different species of animals could also be differentiated in a similar way. S. B. S.

Distribution of Salts between Saturated Aqueous and Moist Gluten. ALB. J. J. VANDEVELDE and L. BOSMANS (*Bull. Soc. chim. Belg.*, 1912, 26, 249—254).—Saturated solutions of salts (40 c.c.) and moist gluten (5 grams, containing 3·4 grams of water) were kept at 37° for one, two, and three weeks, and the amounts of salts in the solution and in the gluten estimated. The dry matter of the gluten remained unchanged. The weight of the moist gluten diminishes, the absorption of salt being coincident with loss of water.

By dividing the percentages of salt in solution by the percentages in the moist gluten, it is shown that chlorides and nitrates of alkalis give higher coefficients than those of the alkaline earths. With potassium salts the coefficient of the nitrate is lower than that of the chloride, and the sulphate lower than the nitrate. In the case of sodium salts, the relations are reversed. The chlorides and nitrates of barium, strontium, and calcium show only slight differences. The highest coefficients obtained are those of ammonium and magnesium sulphates, both of which are important in the fractional precipitation of proteins. N. H. J. M.

Constitution of the Colouring Matter of Blood. III. OSCAR PILOTY and SIEGFRIED J. THANNHAUSER (*Annalen*, 1912, 390, 191—209).—The determination of the constitution of the colouring matter of the blood is rendered difficult by the fact that by the degradation of the substance, whilst one half of the molecule is obtained in well-defined compounds (pyrroles and their carboxylic acids), the other half is obtained in the form of the amorphous, ill-defined hæmatopyrrolidinic acid. It is fortunate, therefore, that bilirubin (obtained from the gall-stones of the ox) yields by its degradation a substance, bilic acid, which is quite analogous to hæmatopyrrolidinic acid, but is crystalline and well-defined. Since it is extremely probable that the colouring matter of the bile is directly produced in the liver from the colouring matter of the blood, the authors hope, by determining the constitution of bilic acid, to secure a tool whereby the constitution of hæmatopyrrolidinic acid, and ultimately that of the colouring matter of the blood, may be fashioned with certainty.

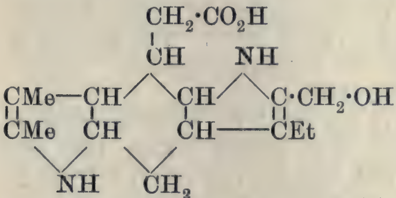
By fusion with potassium hydroxide and a little water at 200° and finally at 370°, bilirubin yields an oil which is shown to contain *bis*-2 : 3-*dimethylpyrrole*, $C_{12}H_{18}N_2$, m. p. 84—85°, colourless crystals (*picrate*, m. p. 148°), and 2 : 3 : 4-*trimethylpyrrole*, which has only been isolated as the *picrate*, $C_7H_{11}N,C_6H_2(NO_2)_3{\cdot}OH$, m. p. 140°, on account of lack of material. The synthesis of these two pyrrole derivatives will be described in a future communication.

By reduction on the water-bath with hydriodic acid (D 1·96) and

phosphonium iodide in the presence of glacial acetic acid, bilirubin yields, in addition to a very small quantity of a base (unexamined), which is volatile with steam, *bilic acid*, and an acid which, being isomeric with phonopyrrolecarboxylic acid, is called iso*phonopyrrolecarboxylic acid.*

Bilic acid, $C_{17}H_{26}O_3N_2$, m. p. 187°, colourless plates, does not respond to the pine-shaving test, and does not develop a red coloration with *p*-dimethylaminobenzaldehyde. The acid is moderately soluble in water, forming a solution which foams on shaking, liberates carbon dioxide from sodium carbonate, and forms an amorphous picrate.

Bilic acid yields hæmatic acid and methylethylmaleimide by oxidation with chromic and dilute sulphuric acids at 50—60°, or by treatment with nitrous acid in warm dilute sulphuric acid. This fact, taken in conjunction with the fact that bilic acid yields, by fusion with potassium hydroxide, a mixture of pyrroles which does not contain hæmopyrrole (thereby showing that an oxygen atom in bilic acid must be present in a hydroxyl group in the α-position to an imino-group) is strong evidence in favour of the annexed formula of bilic acid.



The authors show that zinc hæmatopyrrolidinate also yields hæmatic acid and methylethylmaleimide by oxidation with chromic and dilute sulphuric acids at about 50°. Consequently, the constitution of hæmatopyrrolidinic acid previously suggested is to be replaced by one differing from that of bilic acid only by containing a methyl group in place of the $CH_2 \cdot OH$.

iso*Phonopyrrolecarboxylic acid*, $C_9H_{13}O_2N$, m. p. 126—127°, colourless, prismatic needles, responds to the pine-shaving test, forms a *picrate*, m. p. 146°, and is converted by sodium nitrite and dilute sulphuric acid at about 50° into the semi-oxime of hæmatic acid, decomp. 210°, identical with that obtained from xanthopyrrolecarboxylic acid; the semi-oxime yields hæmatic acid by hydrolysis with boiling dilute sulphuric acid. *iso*Phonopyrrolecarboxylic acid, therefore, is 2 : 4-dimethylpyrrole-3-propionic acid,

$$\begin{matrix} NH \cdot CMe \\ | \\ CH{:}CMe \end{matrix} \!\!> C \cdot CH_2 \cdot CH_2 \cdot CO_2H.$$

C. S.

A Comparison of Paranuclein Split off from Caseinogen with a Synthetic Paranuclein based on Immunity Reactions. FREDERICK P. GAY and T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 12, 233—238).—Paranuclein and synthetic paranuclein-*A* (Robertson) derived from the products of complete peptic digestion of caseinogen and synthesised by the action of pepsin at 36° are interchangeable, as tested by reactions of anaphylaxis and of alexin fixation with an anti-caseinogen serum. They have identical and specific antigenic properties that are not present in the original peptic digestion product. W. D. H.

Electrochemistry of Proteins. VIII. The Dissociation of Solutions of the Sulphate and Chloride of Protamine (Salmine). THORBURN BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1912, 16, 382—394. Compare Abstr., 1911, i, 933).—The proteins hitherto investigated by the author have been either predominantly acidic (caseinogen, serum-globulin) or feebly basic (ovimucoid). The protein salmine here considered is of the predominantly basic type.

Salmine sulphate was prepared from the sperm of Pacific salmon by Kossel's method (Abstr., 1898, i, 715). The chloride was obtained from it by interaction with barium chloride. The author's products were not analysed.

The dissociation of these salts obeys Ostwald's law for a binary electrolyte in the special form devised by the author. The number of ions is therefore two or a multiple of two.

In the case of the sulphate no further evidence could be obtained because the substance separates as an oily phase on cooling and does not lend itself to cryoscopic measurements.

According to the conductivity, a $\frac{1}{2}$% solution of salmine chloride is almost completely ionised. The freezing point of this solution indicates a concentration (molecular + ionic) of $M/46$. The amount of hydrochloric acid present according to the empirical formula

$$C_{30}H_{57}N_{17}O_6,4HCl$$

(Kossel) is $N/45$. Hence one ion is produced for every molecule of hydrogen chloride in the compound. The author argues that one molecule of salmine chloride must yield four ions, and as it behaves as a binary electrolyte, these ions must be capable of combining in pairs. From the value of the conductivity constant ($\rho = 4$ approximately), it is deduced that each ion must be quadrivalent.

Accepting the suggestion of Kossel and Dakin that there are twelve arginine radicles and twelve hydrogen chloride molecules in a salmine hydrochloride molecule, the author supposes that half the arginine radicles combine with the acid to form the anions, whilst the remainder of the arginine radicles form the corresponding cations. In other words, salmine hydrochloride dissociates into twelve quadrivalent protein ions.

The dissociation is formulated on the same lines as that of ovimucoid hydrochloride (*loc. cit.*). R. J. C.

Nature of Animal Lactase. MARJORY STEPHENSON (*Bio.-Chem. J.*, 1912, 6, 250—254).—E. F. Armstrong showed that there are two kinds of lactase, one, galacto-lactase, inhibited only by galactose, and the other, gluco-lactase, inhibited only by dextrose. The lactase in the intestine of animals belongs to the latter class. W. D. H.

Syntheses of Alkyl Glucosides by means of Emulsin: β-Methyl Glucoside, β-Ethyl Glucoside, and β-Propyl Glucoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 155, 86—88. Compare this vol., i, 522, 672).—Emulsin acting on a solution of dextrose in 85% methyl alcohol in the course of thirty-four days converts 79% of the sugar into β-methylglucoside, m. p. 102—104°, $[\alpha]_D$ − 32·06°, which in aqueous solution is completely re-hydrolysed by emulsin.

The authors have succeeded in obtaining β-ethyl glucoside in a crystalline form (compare Königs and Knorr, Abstr., 1901, i, 369) from the syrupy product obtained by a similar reaction by dissolving it in cold pure acetone and keeping the solution. It crystallises in white, felted masses, m. p. 73°, $[\alpha]_D$ $-33·38°$. It is very hygroscopic, but its aqueous solution does not reduce Fehling's solution.

β-Propyl glucoside similarly prepared crystallises in silky tufts, $[\alpha]_D$ $-34·9°$. W. G.

The Supposed Specific Action of Phenolase. ALEXIS BACH and (Mlle.) V. MARYANOVITCH (*Arch. Sci. phys. nat.*, 1912, [iv], **33**, 483—497; *Biochem. Zeitsch.*, 1912, **42**, 417—431).—The influence exercised by salts (calcium chloride and acetate, zinc sulphate and acetate, manganese sulphate and acetate, aluminium sulphate) on phenolase when acting on different substrates (guaiacol, quinol, pyrogallol, orcinol, α-naphthol + p-phenylenediamine) varies with the nature of the substrate. Thus calcium chloride retards the oxidation of guaiacol and of pyrogallol and accelerates oxidation of the other phenols mentioned. Zinc sulphate accelerates the oxidation of guaiacol and of the mixture α-naphthol + p-phenylenediamine, but retards action in all other cases. There is no direct relation between the hydrolysis of the salts and their action.

The salts have a similar specific influence on the oxidation of the phenols by themselves in the absence of phenolase. It is therefore unnecessary to attribute the varying behaviour of phenolase to the presence in it of several specific ferments. All attempts to isolate such specific enzymes have failed, and the specific differences observed are to be attributed to the formation of complexes between the salt and the phenol which are more or less readily oxidised, as the case may be, than the original phenol.

The inability of the oxydase of the potato to act on guaiacol is due, not to the absence of a specific oxydase, but to the ease with which the products of oxidation of guaiacol are reduced by a reducing enzyme also present in the potato. The products of oxidation of quinol or of pyrogallol are not so easily reduced.

The inability of certain preparations of phenolase to oxidise orcinol is to be attributed to the absence of salts of alkaline reaction, the presence of which is essential for the spontaneous oxidation of orcinol.

There is thus no evidence that phenolase is in any way specific, or that a different oxydase is required to oxidise polyhydroxyphenols than for monohydroxyphenols. E. F. A.

Relations of Isomorphism in Organometallic Compounds. II. Derivatives of Tervalent Elements. PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 595—602. Compare this vol., i, 524).—The author has studied the elements of the nitrogen family by means of their compounds corresponding with triphenylamine, and his results bear out the facts already known as to the subdivision of this family, nitrogen and phosphorus going together, then arsenic and antimony, whilst bismuth stands somewhat apart.

Triphenylamine and triphenylphosphine both crystallise in the monoclinic system, triphenylarsine and triphenylstibine in the triclinic, whilst triphenylbismuthine crystallises in the monoclinic system, but in forms fundamentally different from the amine and stibine. A study of their molecular volumes groups them in the same way. Further, the author has studied the solidification temperatures of mixtures of these substances and plotted the corresponding curves, and the results of this thermal analysis are in accord with the chemical study of this group of elements. W. G.

Aromatic Arsenic Compounds. I. *p*-Nitrosophenylarsinic Acid. P. KARRER (*Ber.*, 1912, **45**, 2065—2068).—If a neutral or feebly alkaline solution of atoxyl is oxidised with a neutralised solution of permonosulphuric acid, the resultant liquid on acidifying deposits pale yellow needles of p-*nitrosophenylarsinic acid*,

$$NO\cdot C_6H_4\cdot AsO(OH)_2.$$

This substance shows all the typical nitroso-reactions; on heating it turns brown at 180°, and chars without melting, but when rapidly heated it explodes; it has no medicinal value. Sodium hyposulphite reduces it to *pp'*-diaminoarsenobenzene (Ehrlich and Bertheim, Abstr., 1911, i, 593), whilst milder reducing agents, such as sulphurous acid reduce it to *p*-aminophenylarsenic oxide.

Clauser's method for the estimation of nitrogen (Abstr., 1901, ii, 422) gives satisfactory results with *p*-nitrosophenylarsinic acid.

D. F. T.

Action of the Acetal of Propargaldehyde on Mercuriated Amines. FRITZ REITZENSTEIN and GOTTLIEB BONITSCH (*J. pr. Chem.*, 1912, **86**, [ii], 73—81).—The authors have attempted to prepare the compound, $OAc\cdot Hg\cdot C_6H_4\cdot NH\cdot CH\!:\!CH\cdot CH\!:\!N\cdot C_6H_4\cdot Hg\cdot OAc$, by the condensation of *p*-aminophenylmercuric acetate with the acetal of propargaldehyde, but these attempts have not met with success.

When heated on the water-bath with the acetal of β-ethoxyacraldehyde, *p*-aminophenylmercuric chloride yields an orange-red *substance*, probably $HgCl\cdot C_6H_4\cdot NH\cdot CH\!:\!CH\cdot CH(OEt)_2$, which darkens at 160° and has m. p. 190°.

Diazotised 3''-amino-4:4'-tetramethyldiaminotriphenylmethane combines with phenol dissolved in aqueous sodium hydroxide, yielding a dark yellow *sodium* salt of 4:4'-*tetramethyldiaminotriphenylmethane-3''-azophenol*, $ONa\cdot C_6H_4\cdot N\!:\!N\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2$, and with *o*-hydroxyphenylmercuric chloride to form a dark green *substance*, possibly $HgCl\cdot C_6H_3(OH)\cdot N\!:\!N\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2$.

The interaction of *o*-aminophenylmercuric acetate and dinitrophenylpyridinum chloride in acetone solution yields a reddish-brown *substance*, which probably has the constitution:

$$OAc\cdot Hg\cdot C_6H_4\cdot N\!:\!CH\cdot CH\!:\!CH\cdot CH\!:\!CH\cdot \underset{H\quad Cl}{NH}\cdot C_6H_4\cdot Hg\cdot NH\cdot C_6H_3(NO_2)_2.$$

F. B.

Organic Chemistry.

Action of Ultraviolet Rays on Gaseous Hydrocarbons. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, **155**, 521—522).—A claim for priority over Landau (*ibid.*, 403) in the study of the action of light on saturated hydrocarbons. The authors briefly recapitulate the results previously recorded by them (compare *Rev. gén. des Sciences*, 1911, 330). W. G.

Optical Investigation of Hungarian Naphtha. MICHAEL A. RAKUSIN and E. LASLO (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1076).—A sample of Hungarian naphtha, D^{15} 0·8348, gave a carbonisation constant, *K*, greater than 0·25%. Seven fractions showed rotations of 0—1·6 saccharimetric divisions, and gave the ordinary coloration with Tschugaeff's cholesterol reagent. T. H. P.

Decomposition of Methylene Iodide and its Bearing on the Constitution of Steel. EDWARD D. CAMPBELL and HENRY S. RAWDON (*J. Amer. Chem. Soc.*, 1912, **34**, 1159—1168).—The hypothesis recently advanced by Sargent (this vol., i, 674), that the mixture of hydrocarbons obtained on dissolving steel in hydrochloric acid may be explained by the decomposition of a single carbide of iron, CFe_3, into methylene which polymerises into the olefines, is strongly criticised with regard to its originality and its truth. The old assumption that methylene, if liberated in acid solution in presence of nascent hydrogen, would either be completely reduced to methane or, if polymerisation took place, this would not proceed beyond the formation of ethylene, which latter might be reduced to methane, is now confirmed. Methylene iodide was reduced by means of a zinc–copper couple, and found to yield no hydrocarbon with more than two carbon atoms, even in the presence of ferrous chloride. In one experiment, 16·798 grams of methylene iodide and hydrochloric acid acting on an excess of zinc until all action had ceased, yielded 16·15 litres of gas, which contained 64·6 c.c. of ethylene and 1033·6 c.c. of methane, leaving 17·4% of the carbon in the form of ethyl and ethylene haloids.

The authors plead for the recognition of the possibility of there being many complex carbides of iron in which the property of carbon to link up with carbon is preserved. Their experience shows that the conception that in steel the main part of the iron holds in solution a number of carbides the constitution of which depends on the carbon concentration and heat treatment, is not contrary to fact. J. C. W.

Preparation of $\beta\gamma$-Dimethyl-$\Delta^{\alpha\gamma}$-butadiene. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 246660, 249030, 250086).—The preparation of $\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene from pinacone can be effected by dehydration with potassium hydrogen sulphate or acid salts of di- or poly-sulphonic acids; pinacone (500 parts) is intimately mixed with the salt (750 parts), the mixture heated at 140—150°, and the product

separated by fractional distillation. Toluidine hydrogen sulphate or other hydrogen salts of sulphuric acid can be employed for this reaction, as can also neutral salts having an acid reaction such as the alums, the sulphates of copper, iron, aluminium, etc. F. M. G. M.

Preparation of Isoprene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 246241. Compare Abstr., 1906, i, 394).—When methyl*iso*propenylcarbinol, $CH_2:CMe \cdot CHMe \cdot OH$, is heated slowly to 130—150° with 10 parts of anhydrous oxalic acid, water is eliminated and isoprene formed. The oxalic acid can be replaced by zinc chloride, hydrogen potassium sulphate, or similar dehydrating agents. F. M. G. M.

Preparation of Erythrene and Isoprene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247145. Compare Abstr., 1911, i, 598).—When the quaternary halogen ammonium bases of general formula $CH_3 \cdot CHX \cdot CHY \cdot CH_2 \cdot NMe_3X$ (where X is a halogen atom and Y hydrogen or methyl) are distilled with either alkaline hydroxides or alkaline earths, they furnish erythrene or isoprene according to the equation: $CH_3 \cdot CHX \cdot CHY \cdot CH_2 \cdot NMe_3X + 2KOH = 2KX + CH_2:CH \cdot CY:CH_2 + NMe_3 + 2H_2O$.

The *compound*, $HO \cdot CHMe \cdot CHMe \cdot CH_2 \cdot NMe_3Br$, is a colourless, crystalline mass, whereas the halogenated bases are usually viscid, brown syrups. F. M. G. M.

A Method for the Exact Determination of the Position of the Hydroxyl Groups in Polyhydroxy-compounds. JACOB BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 216—223).—The experiments of Böeseken and van Rossem (this vol., ii, 147) have shown that, of the polyhydroxybenzenes, only the ortho-derivatives exert a very great positive influence on the conductivity of boric acid.

Simple glycols do not increase the conductivity, and it is assumed that the hydroxyl groups repel one another, a similar condition occurring in sucrose. α-Dextrose increases the conductivity at first, the value then falling, whilst β-dextrose has little influence at first, the conductivity then increasing until the same final value is reached. This behaviour gives a clue to the configuration of the two isomerides. C. H. D.

Ethoxides of Calcium and Barium. ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1912, [viii], **26**, 209—227).—A more detailed account of work published already (this vol., i, 67).

Calcium ethoxide, prepared by Doby's method (Abstr., 1903, i, 546), develops 40·27 Cal. on neutralisation by hydrochloric acid, whence its heat of formation is 93·93 Cal. That of its molecular compound with 2 mols. of ethyl alcohol is 102·48 Cal., whilst solution of calcium in excess of alcohol develops 101·04 Cal. The last figure is very close to Guntz's result for the solution of calcium in water, namely, 101·12 Cal. T. A. H.

Oxidation of Propylene Glycol. I. The Action of Alkaline Permanganate Giving Carbonic, Acetic, and Oxalic Acids. WILLIAM LLOYD EVANS and EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1912, **34**, 1086—1104).—The paper commences with a brief résumé of the results of previous investigations under various conditions.

The action of an alkaline solution of potassium permanganate on aqueous propylene glycol at room temperature gives as sole end products, carbon dioxide, acetic and oxalic acids; an increase in the proportion of alkali raises the ratio of oxalic to acetic acid (compare Cochenhausen, Abstr., 1899, i, 251); raising the temperature increases the proportion of carbon dioxide. The authors conclude that there must be at least three reactions (exclusive of any intermediate ones), namely: (*a*) $HO\cdot CHMe\cdot CH_2\cdot OH + 4O \longrightarrow AcOH + CO_2 + 2H_2O$; (*b*) $HO\cdot CHMe\cdot CH_2\cdot OH + 7O \longrightarrow C_2O_4H_2 + CO_2 + 3H_2O$;

(*c*) $HO\cdot CHMe\cdot CH_2\cdot OH + 8O \longrightarrow 3CO_2 + 4H_2O$.

Similar experiments on the oxidation of lactic and pyruvic acids yielded like results; acetic and oxalic acids and carbon dioxide are formed, the last again being in excess of that expected from one carbon atom of each oxidised molecule.

These results are discussed in the light of Nef's dissociation theory (Abstr., 1905, i, 3). Attention is also drawn to the fact that the oxidation of lactic acid is not as simple a process as is assumed by Ulzer and Seidel (Abstr., 1897, ii, 389) in their process for the estimation of this acid. D. F. T.

Preparation of Glycols from Dihalogenbutanes and their Homologues. CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.-P. 246572. Compare Abstr., 1876, 64; 1878, 845, 850).—Various methods of preparing glycols have been previously described; the following procedure is now advocated.

$\beta\gamma$-Dibromo*iso*pentane (23 parts) is added to a solution of sodium hydroxide (10 parts in 500 parts of water) and allowed to remain several days at the ordinary temperature with frequent stirring; the solution is neutralised, a "salting out" agent introduced, and the glycol (8·5 parts) isolated by extraction with ether.

$\beta\gamma$-Butanediol (7 to 8 parts) is obtained when $\beta\gamma$-dichlorobutane (12·7 parts) is added to a mixture of calcium hydroxide (10 parts) with water (500 parts) and heated at about 75° until the reaction is complete. F. M. G. M.

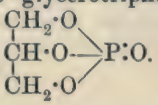
Action of Concentrated Phosphoric Acid on Glycerol. II. ANGELO CONTARDI (*Gazzetta*, 1912, **42**, ii, 270—282).—Consideration of previous results (compare Carré, Abstr., 1904, i, 133, 215; 1905, i, 184; 1911, i, 263; Contardi, Abstr., 1910, i, 157, 609) would lead to the conclusion that in the esterification of polyhydric alcohols with phosphoric acid, when the number of hydroxyls is sufficiently large and no dehydration intervenes, the reaction occurs preferably between 1 mol. of alcohol and 1 mol. of the acid. The reaction between glycerol or other polyhydric alcohol and phosphoric acid seems, however, to be more complicated than is generally assumed; thus, when

equimolecular proportions of glycerol and phosphoric acid are mixed, esterification does not proceed solely molecule for molecule, the triphosphoric ester, $C_3H_5(PO_4H_2)_3$, being always formed in considerable amount; this ester alone is obtained when 1 mol. of glycerol or triacetin is esterified with 3 mols. of phosphoric acid.

When an equimolecular mixture of anhydrous glycerol and phosphoric acid is heated at 130° for ten to twelve hours and under 18—20 mm. pressure, one-half of the phosphoric acid is transformed into glycerotriphosphoric acid, and the other half, in the first phase, into ordinary α- and β-glycerophosphoric acid,

$$[OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot PO_4H_2$$

and $OH\cdot CH_2\cdot CH(PO_4H_2)\cdot CH_2\cdot OH]$; one-third of the glycerol takes no part in the reaction, which may be represented thus: $6C_3H_8O_3 + 6H_3PO_4 = C_3H_{11}O_{12}P_3 + 2C_3H_8O_3 + 3C_3H_9O_6P + 6H_2O$. This result does not seem to agree with Carré's observation that an equimolecular mixture of glycerol and phosphoric acid is transformed quantitatively into the neutral tri-ester in the vacuum of a mercury pump. It is found that esterification of 1 mol. of glycerol with 3 mols. of phosphoric acid, and treatment of the final glycerotriphosphoric acid obtained with 2 mols. of anhydrous glycerol under the conditions employed by Carré, gives an almost quantitative yield of the solid, neutral ether; hence the glycerotriphosphoric acid loses 2 mols. H_2O, giving the tri-ether,



T. H. P.

Preparation of Epichlorohydrin from Dichlorohydrin. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 246242).—It is found that the potassium hydroxide usually employed in the preparation of epichlorohydrin (from dichlorohydrin) can be replaced by either alkali carbonates or alkaline earth hydroxides. The distillation of dichlorohydrin at 80° and 135 mm. with twice the quantity of calcium hydroxide indicated by theory furnished a 95% yield of epichlorohydrin, whilst with sodium carbonate an 85% yield was obtained F. M. G. M.

The Lecithin of Egg-Yolk. J. D. RIEDEL (*Chem. Zentr.*, 1912, i, 1794; from *Riedel's Ber.*, 1912, 24—33).—A purified lecithin has been obtained from egg-yolk, free from cholesterol and foreign albumin, by extraction with cold methyl alcohol. The formula: $OR\cdot CH_2\cdot CR'(OH)\cdot CH_2\cdot PO_3(OH)\cdot C_2H_4\cdot NMe_3\cdot OH$, is proposed for lecithin, R and R′ being aliphatic acyl groups, of which palmitic, stearic, oleic, and linoleic acids have been recognised. C. H. D.

Purification of Ether to be Used as an Anæsthetic. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1912, [vii], 6, 212—213).—Commercial ether is shaken repeatedly with 3% by volume of Denigès' mercuric acid sulphate reagent, until on addition of a fresh quantity of the reagent no precipitate, or only a white precipitate, is formed. The separated ether is filtered and then allowed to remain, with frequent agitation, in contact with excess of quicklime and ground calcium chloride, and

finally redistilled. The purified ether should be kept in full, well-corked bottles. T. A. H.

Methyl Thiolmethyl Ether and the Corresponding Thioethers. JEAN DE LATTRE (*Bull. Soc. chim. Belg.*, 1912, 26, 323—336).—*Methyl thiolmethyl ether*, $CH_3 \cdot O \cdot CH_2 \cdot SH$, was prepared by the action of methyl chloromethyl ether on potassium hydrogen sulphide ($4KHS,H_2O$) at the ordinary temperature. Anhydrous potassium hydrogen sulphide and methyl chloromethyl ether react very slowly in the absence of solvent or in the presence of ether. The thiol has b. p. 52°/15 mm., m. p. −52·4°, D_0^0 1·1018, D_{12}^{12} 1·0738, n_D^{20} 1·4909, mol. wt. (in benzene or glacial acetic acid solution) 154. Water and alkalis decompose it with the formation of thiomethylene. When heated at the boiling point of aniline, it forms trithiomethylene, m. p. 215°, and methyl alcohol. Gaseous hydrogen chloride and hydrogen iodide transform it into trithiomethylene, methyl chloride, and methyl iodide respectively. Addition of an alcoholic solution of mercuric chloride precipitates the *compound*, $OMe \cdot CH_2S,HgCl$, which decomposes when heated, whilst yellow mercuric oxide converts it in alcoholic solution into the *mercaptide*, $(CH_3 \cdot O \cdot CH_2 \cdot S)_2Hg$. Benzoylation in pyridine solution yields the corresponding *benzoyl* derivative, b. p. 146°/15 mm., D_0^0 1·2171, $D_{21\cdot6}^{21\cdot6}$ 1·2007, $n_D^{21\cdot6}$ 1·5760. Application of the Schotten-Baumann method yields principally trithiomethylene with small quantities of the above compound, whilst, when boiled with benzoyl chloride, the thiol yields trithiomethylene and methyl benzoate. Acetyl chloride in the presence of pyridine converts the thiol into the corresponding *acetyl* derivative, b. p. 94°/15 mm., D_0^0 1·1978, D_{27}^{27} 1·1860, n_D^{27} 1·5178.

An attempt to prepare methyl thiolmethyl ether by the action of methyl chloromethyl ether on an alcoholic solution of potassium hydrogen sulphide led to the isolation of a *thiomethylene*, $(CH_2S)_n$, m. p. 123—124°.

Dimethyl ether sulphide, $(CH_3 \cdot O \cdot CH_2)_2S$, prepared by the action of methyl chloromethyl ether on potassium sulphide ($2K_2S,H_2O$) at the ordinary temperature, has b. p. 62°/15 mm., D_0^0 1·0671, $D_{21\cdot5}^{21\cdot5}$ 1·0418, $n_D^{12\cdot5}$ 1·4575. When heated with methyl iodide, at the ordinary temperature or at 80°, it forms trimethylsulphonium iodide and oxymethylene.

Dimethyl ether disulphide, $(CH_3 \cdot O \cdot CH_2)_2S_2$, is formed simultaneously with some monosulphide and *trisulphide* by cautiously heating methyl chloromethyl ether with potassium disulphide ($2K_2S_2,H_2O$). It has b. p. 115°/15 mm., D_0^0 1·2086, D_{22}^{22} 1·1881, n_D^{22} 1·5290. When the above substances are allowed to react in the cold, only the monosulphide, $(CH_3 \cdot O \cdot CH_2)_2S$, is obtained. The latter substance, at its boiling point, does not react with sulphur. If, however, potassium sulphide ($2K_2S,H_2O$) is added, it combines with the sulphur, giving excellent yields of disulphide.

Phenyl methoxymethyl sulphide, $C_6H_5 \cdot S \cdot CH_2 \cdot OMe$, obtained by the action of magnesium phenyl bromide on dimethyl ether disulphide (compare Wuyts, Abstr., 1906, i, 257), is a colourless liquid, b. p. 108°/12 mm., D_0^0 1·1214, D_{16}^{16} 1·1047, n_D^{16} 1·5707. H. W.

The Hydrolytic Action of Glycine on Ethyl Butyrate. S. LIEBOWITZ (*J. Amer. Chem. Soc.*, 1912, **34**, 1111—1113. Compare Falk and Nelson, this vol., i, 522).—Experiments at temperatures from 20° to 40° indicate that glycine exerts a marked hydrolytic effect on aqueous solutions of ethyl butyrate; there is a rough parallelism between the amount of action and the amounts of ester or of glycine used, the extent of the hydrolysis being measured when far from completion. The replacement of water by *N*-sodium chloride solution as medium had no effect. D. F. T.

Preparation of Carbonic Ester of Tertiary Alcohols. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 246298).—It is found that amylene carbamate (this vol., i, 541) or similar esters can be readily prepared by treating the sodium derivative of the alcohol with carbamyl chloride in dry benzene, or by employing the free alcohol in the presence of an acid eliminating agent, such as dimethylaniline. F. M. G. M.

Action of Alcoholic Ammonia on αβ-Dibromopropionic Acid. WILLIAM H. WARREN (*J. Amer. Chem. Soc.*, 1912, **34**, 1082—1086). —The action of ammonia on αβ-dibromopropionic acid is known to yield αβ-diaminopropionic acid (Klebs, Abstr., 1894, i, 439) and β-amino-α-hydroxypropionic acid (*iso*serine: Neuberg and Ascher, Abstr., 1907, i, 1014). If, however, a 12·5% solution of ammonia in absolute alcohol is allowed to react in the cold with an alcoholic solution of αβ-dibromopropionic acid, the sole organic product appears to be ammonium α-bromoacrylate; this was separated from the mixture obtained after evaporation by treating with silver sulphate to convert the ammonium bromide into the sulphate, from which the ammonium α-bromoacrylate, plates, m. p. 148° (decomp.), is easily separable by alcohol; the identity of this substance was confirmed by conversion into the silver salt and into the free acid, which from its m. p. (69°) must be the α-isomeride (Wagner and Tollens, this Journ., 1874, 680).

When the interaction of alcoholic ammonia and dibromopropionic acid is assisted by heat, no ammonium α-bromoacrylate is obtained, but some αβ-diaminopropionic acid. The formation of the former compound in the above reaction may explain the poor yields of αβ-diaminopropionic acid obtained by earlier investigators, as α-bromoacrylic acid decomposes exceedingly readily, giving a gelatinous product. D. F. T.

Action of the Chlorides of α-Alkyloxy-acids on Organo-Metallic Derivatives of Zinc. II. EDMOND E. BLAISE and L. PICARD (*Ann. Chim. Phys.*, 1912, [viii], **26**, 258—288).—In the previous memoir (this vol., i, 232) it was shown that the products of this reaction may be either alkyloxy-ketones or ethers, and the influence on the reaction of the radicle in the organo-metallic compound used was investigated. The present paper deals with the influence of the alkyloxy-residue of the acid chloride.

*iso*Butoxyacetic acid, $C_4H_9\cdot O\cdot CH_2\cdot CO_2H$, b. p. 118—119°/16 mm. or 105—106°/8 mm., prepared by the action of *iso*butyl chloroacetate

on sodium *iso*butoxide, is a viscous liquid, readily soluble in water. The *ethyl* ester, b. p. 69°/10 mm., is a mobile liquid with a fruity odour. The *chloride*, b. p. 48°/10 mm., is a mobile liquid of suffocating odour produced along with some *chloromethyl* iso*butyl ether*, b. p. 26°/12 mm., and a little iso*butyl* iso*butoxyacetate*, b. p. 89—90°/10 mm., by the action of thionyl chloride on the acid. The *amide*, m. p. 78°, crystallises from a mixture of benzene and light petroleum in needles. The *anilide*, m. p. 45°, forms colourless needles from light petroleum. The p-*toluidide*, m. p. 43°, crystallises from alcohol, and the *phenylhydrazide*, m. p. 92°, separates from ether on addition of light petroleum in slender needles. The condensation of the chloride with zinc ethyl iodide has been described already (Abstr., 1911, i, 175); the resulting *iso*butoxymethyl ethyl ketone on reduction with sodium yields the corresponding *alcohol*, $C_4H_9O\cdot CH_2\cdot CH(OH)\cdot C_2H_5$, b. p. 72—73°/14 mm., whilst the ketoxime (*loc. cit.*) is reduced by sodium amalgam, giving ammonia, *iso*butyl alcohol (phenylurethane, m. p. 85·5—86°), *sec.*-butylamine (*di*-sec.-*butyloxamide*, needles, m. p. 160° approx.), and *β-amino-α*-iso*butoxybutane*,

$$CHMe_2\cdot CH_2\cdot O\cdot CH_2\cdot CH(NH_2)\cdot C_2H_5,$$

b. p. 167°/760 mm. The last-mentioned substance is a viscous liquid, sparingly soluble in water, and has an odour recalling that of piperidine. The *sulphate* forms colourless spangles, and the *picrate*, m. p. 101°, lemon-yellow spangles. The *benzoyl* derivative has m. p. 40°, b. p. 206°/19 mm., and the *carbamide*,

$$NH_2\cdot CO\cdot NH\cdot CHEt\cdot CH_2\cdot O\cdot C_4H_9,$$

m. p. 92°, forms brilliant spangles from a mixture of benzene and light petroleum. On addition of hydrochloric acid, amino*iso*butoxybutane gives *aminobutyl alchhol hydrochloride*, $C_2H_5\cdot CH(CH_2\cdot OH)\cdot NH_2,HCl$, deliquescent needles, the *platinichloride* of which forms yellow lamellæ, m. p. 189—190° (decomp.).

Phenoxymethyl ethyl ketone, the product of the action of zinc ethyl iodide on phenoxyacetyl chloride (*loc. cit.*), gives with hydrazine hydrate the corresponding *azine*, m. p. 72°, crystallising in needles. With hydroxylamine only a small yield of the *ketoxime*, m. p. 69°, needles, is obtained, due to partial decomposition of the ketone, with the liberation of phenol, and on reduction the oxime yields *sec.*-butylamine and phenol.

Ethyl α-bromohexoate reacts with sodium ethoxide to form ethyl α-ethoxyhexoate as chief product, with a small amount of a second *ester*, $C_{16}H_{30}O_4$, b. p. 149°/7 mm., yielding on hydrolysis a liquid *acid*, which readily gives an *anhydride*, b. p. 175—180°/9 mm., from which an *anilide*, m. p. 154°, in brilliant crystals may be obtained; this acid is probably *αα-di*-n-*butylsuccinic acid*. α-Ethoxyhexoic acid, b. p. 124·5°/10 mm., prepared from the *ethyl* ester, b. p. 93°/16 mm. (see above), yields crystalline *copper* and *calcium* salts, and with thionyl chloride furnishes the acid chloride (Abstr., 1911, i, 260), from which the corresponding *amide*, brilliant spangles, m. p. 78°, *anilide*, needles, m. p. 57°, and p-*toluidide*, m. p. 34°, b. p. 185°/9 mm., were prepared. On treating α-ethoxyhexoyl chloride with zinc ethyl iodide no ketone is produced, the only condensation product being γ-ethoxyheptane (*loc. cit.*), which, on treatment with hydriodic acid, yields *γ-iodoheptane*,

$C_2H_5\cdot[CH_2]_2\cdot CHI\cdot C_2H_5$, b. p. 64·5°/8·5 mm. The latter with moist silver oxide furnishes a small amount of *heptyl ether*,

$$C_4H_9\cdot CHEt\cdot O\cdot CHEt\cdot C_4H_9,$$

b. p. 106°/10 mm., with *γ-hydroxyheptane*, b. p. 156·5—157°/760 mm. as the chief product. The *acetate* of this, b. p. 53—54°/8 mm., is a pleasant-smelling liquid. T. A. H.

Solubilities of the Lead Salts of the Higher Fatty Acids in Ether and in Light Petroleum. G. B. NEAVE (*Analyst*, 1912, 37, 399—400).—Whereas lead oleate is readily soluble in both liquids, 100 c.c. of ether at 20° dissolve of lead heptoate 0·2397, of lead octoate 0·0938, of lead nonoate 0·1115, and of lead decoate only 0·0290 gram; lead myristate, lead laurate, lead palmitate, and lead stearate are practically insoluble. At the boiling point is dissolved of lead decoate 1·3640, of lead heptoate 1·4900, of lead octoate 0·5460, of lead nonoate 0·2404, of lead decoate 0·4285, of lead myristate 0·0555, of lead laurate 0·0205, and of lead palmitate 0·0261 gram; lead stearate is insoluble.

In light petroleum (b. p. 40—60°) at 20° they are practically insoluble, except the heptoate, which dissolves to the extent of 0·0200 gram. [The solubility of lead decoate at 20° in either solvent is not recorded.] At the boiling point the solubilities are as follows: Lead decoate 0·0608, lead heptoate 0·0528, lead octoate 0·0384, lead nonoate 0·0450, lead decoate 0·0170, lead myristate 0·0210 (lead laurate and palmitate are practically insoluble), and lead stearate 0·017 gram per 100 c.c. L. DE K.

The Formation of *d*-Lactic Acid in Incubated Hen's Eggs. KINZUCHI ANNO (*Zeitsch. physiol. Chem.*, 1912, 80, 237—240).—After three days' incubation an abundant formation of *d*-lactic acid occurs in the white of the hen's egg, whereas only a small quantity can be detected in the yolk. W. D. H.

A Biochemical Method of Preparation of *l*-Tartaric Acid. JACOB BÖESEKEN and H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 212—216).—*l*-Tartaric acid is conveniently prepared by the action of *Aspergillus niger* on racemic acid; the solution after six days at 33—34° gives a maximum *l*-rotation, after which the *l*-acid is slowly consumed. The variety of *Penicillium glaucum* employed had very little selective power, and therefore differed from that used by Pasteur. C. H. D.

Relation between the Iodine Number and the Structure with Acids of the Oleic Series. GIACOMO PONZIO and C. GASTALDI (*Gazzetta*, 1912, 42, ii, 92—95).—The values of the iodine number for undecenoic acid, determined by the Hübl, Wys and Hanuš methods, are very close to the theoretical number, whilst those for crotonic, Δ^{β}-hypogæic, and Δ^{β}-oleic acids are very considerably lower than the theoretical ones. These results are not due to any abnormality in the interaction with iodine of double linkings near to the carboxyl group, but merely to the low velocities with which such

double linkings react. Thus, with Δ^{β}-oleic acid, it is found that increase of the duration of the tests is accompanied by marked increase of the iodine number obtained by all three methods; for instance, the Wys method gave 18·0 after 30 minutes, 37·7 after 3 hours, 76·2 after 12 hours, 84·2 after 24 hours, and 86·8 after 70 hours, the theoretical value being 89·7.

The suggestion is made that the determination of the iodine number may serve as a good method of establishing the position of the double linking in an unsaturated acid. T. H. P.

Degradation of Cholic Acid. III. The Capacity of Cholic Acid Derivatives for Combining with Ozone. OTTO VON FÜRTH and HIROMU ISHIHARA (*Biochem. Zeitsch.*, 1912, **43**, 323—334. Compare Abstr., 1910, i, 606).—The oils obtained by distillation of cholic acid can combine with ozone. If Pregl's formulæ is accepted, the principal distillation product forms an ozonide of the formula $C_{17}H_{24}O_7$. A similar product was obtained by the action of ozone on the product obtained by the fusion of bilianic acid with sodium hydroxide. These ozonides or perozonides show great resistance to various chemical reagents, and have the characteristics of the ozonides of hydroaromatic rather than of aliphatic character. In the substance called dehydrocholon by Pregl, the action of ozone revealed the presence of several double bonds. S. B. S.

Catalytic Hydrogenation of Ketones. GUSTAVE VAVON (*Compt. rend.*, 1912, **155**, 286—288. Compare this vol., i, 628).—Ketones can be readily reduced, by a current of hydrogen in the presence of platinum black, to the corresponding secondary alcohols. Aliphatic, cyclic, aromatic, ethylenic and terpenic ketones, ethyl acetoacetate, and a diketone, acetylacetone, have all been experimented on. Reduction is best carried out in the presence of a solvent varying with the ketone to be reduced. The method is very general, and in most cases the corresponding secondary alcohols are the products, although with some ketones the reduction, if allowed to go on, will proceed to further stages. W. G.

Higher Ketones and Secondary Alcohols Derived from the Amides of Palmitic and Stearic Acids. HUGH RYAN and THOMAS NOLAN (*Proc. Roy. Irish Acad.*, 1912, **30**, *B*, 1—7). The authors have prepared a series of ketones by the action of Grignard's reagents on the amides of palmitic and stearic acids. Reduction by sodium and alcohol transforms these ketones into the corresponding secondary alcohols.

Methyl pentadecyl ketone, $CH_3\cdot CO\cdot C_{15}H_{31}$, m. p. 48°, is obtained by the action of magnesium methyl iodide on palmitamide. Similarly, magnesium phenyl bromide and palmitamide yield *phenyl pentadecyl ketone*, m. p. 59°, the *oxime* of which has m. p. 73—74°. *p*-Tolyl pentadecyl ketone, prepared in an analogous manner, has m. p. 60°; its *phenylhydrazone*, m. p. 54—55°, and its *semicarbazone*, m. p. 114·5°. *a-Naphthyl pentadecyl ketone* has m. p. 48°.

The following ketones were obtained from stearamide: *ethyl hepta-*

decyl ketone, m. p. 57°; *phenyl heptadecyl ketone*, m. p. 64° (*phenylhydrazone*, m. p. 54°); p-*tolyl heptadecyl ketone*, m. p. 66—67°; *a-naphthyl heptadecyl ketone*, m. p. 53—54°. An attempt to prepare the phenylhydrazone of the latter was unsuccessful.

p-*Tolylpentadecylcarbinol*, $CH_3\cdot C_6H_4\cdot CH(OH)\cdot C_{15}H_{31}$, prepared in good yield by the reduction of *p*-tolyl pentadecyl ketone by sodium and alcohol, has m. p. 44—45°. Its *phenylurethane*, m. p. 44°, and its somewhat impure *acetate* were also examined.

Phenylpentadecylcarbinol and *phenylheptadecylcarbinol* have m. p.'s 53° and 59° respectively. The latter substance, when heated with sodium acetate and acetic anhydride, yields an impure *acetate*.

H. W.

The Photochemical Synthesis of Carbohydrates. WALTHER LÖB (*Biochem. Zeitsch.*, 1912, **43**, 434—437).—The author contends that the experimental results of Stoklasa, Sebor, and Zdobnický in their work on the photochemical synthesis of carbohydrates (this vol., i, 606) do not justify the conclusions they have drawn from them.

S. B. S.

Reducing Power of Sugars. NICOLAAS SCHOORL (*Chem. Weekblad*, 1912, **9**, 678—694).—The author gives a summary of work on reduction by the aid of various sugars. He considers that the reduction of alkaline copper solutions by sucrose is a property of the sucrose molecule. A. J. W.

Reducing Power of Sugars (Monosaccharides) and its Bearing on the Definition of these Substances. NICOLAAS SCHOORL (*Chem. Weekblad*, 1912, **9**, 706—711).—The author had found that introduction of a non-oxidised carbon atom between the CO- and CH(OH)-groups in a compound containing the group ·CO·CH(OH)· materially diminishes its power of reducing a weakly alkaline copper solution. He considers that the term "sugars" should include all substances with the group ·CO·CH(OH)·, whether polyhydric alcohols or not. A. J. W.

Enzymatic Phosphate Union. HANS EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1912, **80**, 205—211).—During the alcoholic fermentation, dextrose, lævulose, galactose, and mannose yield intermediate substances which form compounds with phosphates. The hexoses themselves do not form these esters, but dihydroxyacetone, one of the intermediate substances, does. A similar material is formed from dextrin by the action of dilute alkali. W. D. H.

Photolysis of Ketoses by Solar and Ultra-violet Light. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, **155**, 401—403. Compare Abstr., 1910, ii, 813, 114; this vol., ii, 715).—The sugars dihydroxyacetone, erythrulose, lævulose, sorbose, and perseulose are decomposed when their aqueous solutions are exposed in quartz tubes to sunlight. Carbon monoxide with a little carbon dioxide is evolved, and the corresponding alcohol containing one carbon atom less

than the sugar used is formed. The decomposition is slow and more feeble the more complex the sugar used.

On exposure to ultra-violet light from a mercury lamp the same fundamental decomposition occurs, but there are also accessory reactions which result in the evolution of a little hydrogen and sometimes of methane, and in the formation of formaldehyde and non-volatile acids in the solutions. Similar changes occur when the solid sugars are exposed to ultra-violet light. T. A. H.

Hydrolysis of Maltose by Dilute Acids. LADISLAS KOPACZEWSKI (*Bull. Soc. chim.*, 1912, [iv], 11, 850—853).—The existing statements regarding the rate of hydrolysis of maltose by dilute acids being conflicting, the author has re-investigated the question and finds that (1) the hydrolytic activity of acids towards maltose depends on their electrolytic dissociation, and (2) the rate of hydrolysis (*a*) increases rapidly when the concentration of the acid rises above $N/4$, (*b*) increases with the temperature in the case of dilute acids, and (*c*) increases with the concentration of maltose, especially for sulphuric acid. T. A. H.

Influence of Different Acids on the Hydrolysis of Maltose by Maltase. LADISLAS KOPACZEWSKI (*Zeitsch. physiol. Chem.*, 1912, 80, 182—193).—The effect of various acids varies considerably, which shows that concentration of hydrogen ions is not the only important factor in influencing enzymatic activity; the nature of the anions is important also. W. D. H.

Products of the Interaction of Mercuriammonium Chloride and Methyl Iodide. MÁRTON LÖW (*Zeitsch. Kryst. Min.*, 1912, 51, 138—142).—By heating a mixture of 1 mol. of mercuriammonium chloride and 3 mols. of methyl iodide in a sealed glass tube in a water-bath, S. Hajnóci (*Magyar Chem. Foly.*, 1911, 17, 91) obtained the following three substances: (1) methylamine mercuri-iodide as pale yellow prisms and plates; these are orthorhomic with $a:b:c = 0{\cdot}5793:1:0{\cdot}5164$. (2) Dark yellow plates and pyramids, also orthorhombic, $a:b:c = 0{\cdot}6168:1:0{\cdot}7704$, but of unknown composition. (3) Pale yellow crusts and spherical aggregates with probably the composition $NH_4I,2HgI_2$. The three substances differ in their degree of solubility in an aqueous solution of potassium iodide, in nitrobenzene, alcohol, etc., and they also show differences in their behaviour when heated. L. J. S.

Composition of Different Kinds of Silk. XIV. Total and Partial Hydrolysis of the Cocoon of the Ailanthus Spinner and of Tailung Silk. EMIL ABDERHALDEN and RYNGO INOUYE (*Zeitsch. physiol. Chem.*, 1912, 80, 198—204. Compare Abstr., 1911, i, 1050).—Analytical data are given similar to those in the previous papers of the series in reference to the two kinds of Chinese silk mentioned. W. D. H.

Transformation of Ammonium Cyanate into Carbamide. ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1912, 34, 1269—1270).—The author points out that the transformation of ammonium cyanate

into carbamide has been explained for some time, by Willstätter among others, in a simpler way than that proposed by Chattaway (Trans., 1912, 101, 170). The salt decomposes into cyanic acid and ammonia, and, introducing the idea of partial valency, the latter is assumed to attach itself thus:

$$\begin{array}{c} H\cdot N\colon C\colon O \\ |\quad\vdots \\ H\cdot NH_2 \end{array} \longrightarrow \begin{array}{c} H\cdot N\cdot C\colon O \\ |\quad\ | \\ H\ \ NH_2 \end{array}.$$

J. C. W.

The Constitution of the Bimolecular Cyanides of the Fatty Acids. WILHELM BARDROFF (*Monatsh.*, 1912, **33**, 859—871).—Two different structures have been proposed for the bimolecular cyanides of organic acids, namely, $RCO_2\cdot CR(CN)_2$ (Brunner, Abstr., 1895, i, 335, etc.) and $RC(CN){<}^{O}_{O}{>}CR\cdot NC$ (Diels and Pillow, Abstr., 1908, i, 535). To aid decision between these two formulæ the author has investigated the intermediate products in the hydrolysis of these cyanides to homologous tartronic acids (compare Brunner, *loc. cit.*); the results are entirely in favour of the first structure.

If bimolecular acetyl cyanide is cautiously introduced into sulphuric acid (D 1·57) in a freezing mixture and the mixture kept cold for twenty hours, about 50% of the cyanide undergoes conversion into a substance, forming columnar crystals (from alcohol), m. p. 192°. From the molecular weight in aqueous solution and the elementary analysis, the formula is $(C_3H_5O_2N)_2$; as hydrolysis causes the formation of one molecule of acetic acid and two of ammonia, the structure is probably $OAc\cdot CMe(CO\cdot NH_2)_2$, *acetylmethyltartrondiamide*. If this substance is carefully hydrolysed in the cold by potassium hydroxide solution, the acetyl group is removed with formation of a new amide,

$$HO\cdot CMe(CO\cdot NH_2)_2,$$

methyltartrondiamide, m. p. 203·5°, which yields two molecules of ammonia on further hydrolysis.

When bimolecular propionyl cyanide is treated as above with sulphuric acid, there is formed the analogous substance

$$CO_2Et\cdot CEt(CO\cdot NH_2)_2,$$

propionylethyltartrondiamide, tablets, m. p. 168°; it was found impossible to remove the propionyl radicle from this in the manner described for the corresponding acetyl compound. D. F. T.

Action of Phenylthiocarbimide on Carbamide and on Thiocarbamide. A. PIERONI (*Gazzetta*, 1912, **42**, ii, 183—185). —The products of both of these reactions consist of cyanamide and diphenylthiocarbamide:

I. (*a*) $2CO(NH_2)_2 = 2CN\cdot NH_2 + 2H_2O$

and (*b*) $2SCNPh + 2H_2O = H_2S + CO_2 + S\colon C(NHPh)_2$.

II. (*a*) $CS(NH_2)_2 = CN\cdot NH_2 + H_2S$

and (*b*) $2SCNPh + H_2S = CS_2 + S\colon C(NHPh)_2$. T. H. P.

The Direct Nitration of Aliphatic Imino-compounds. ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 207—212. Compare Abstr., 1907, i, 395).—Nitric acid and iminodiacetonitrile, $NH(CH_2\cdot CN)_2$, yield a

crystalline *nitrate*, m. p. 138—140°. If dissolved in absolute nitric acid and evaporated in a vacuum, the product, crystallised from benzene, forms snow-white crystals of *nitroiminodiacetonitrile*,

$$NO_2\cdot N(CH_2\cdot CN)_2.$$

Heating iminodiacetic acid with nitric acid to boiling forms *nitroiminodiacetic acid*, $NO_2\cdot N(CH_2\cdot CO_2H)_2$, which crystallises from ethyl acetate in broad, flat needles, decomp. 153°. The *potassium* salt explodes at 195°. Methyl iminodiacetate forms a *nitrate*, m. p. 198—199°, which is converted by cold nitric acid into the *nitro-compound*, $NO_2\cdot N(CH_2\cdot CO_2Me)_2$, m. p. 63·5°. Iminodiacetamide, $NH(CH_2\cdot CO\cdot NH_2)_2$, forms a *nitrate*, m. p. 206° (decomp.), which is decomposed by absolute nitric acid, yielding nitroiminodiacetic acid.

Iminodiacetimide, $NH{:}(CH_2\cdot CO)_2{:}NH$, forms a *hydrochloride*, decomp. above 180°, and a *nitrate*, both of which contain 1 mol. of acid. Evaporation with nitric acid in a vacuum yields colourless crystals of nitroiminodiacetimide, $NO_2\cdot N{:}(CH_2\cdot CO)_2{:}NH$. In order to determine the position of the nitro-group, *acetyliminodiacetimide*,

$$NAc{:}(CH_2\cdot CO)_2{:}NH,$$

has been prepared by subliming the corresponding diamide, and also by direct acetylation. It has m. p. 167—168°.

Methyliminodiacetic acid, $NMe(CH_2\cdot CO_2H)_2$, yields the *diamide*, m. p. 162—163°, from which the *imide*, $NMe{:}(CH_2\cdot CO)_2{:}NH$, is obtained by sublimation under reduced pressure, and has m. p. 106°. It yields a crystalline *hydrochloride* and *nitrate*, decomposing above 235° and 130° respectively. It has not been found possible to isolate a nitro-derivative.

The phenyl group does not have the same effect as the carboxyl or nitrile groups, as dibenzylamine does not yield a nitroamine.

C. H. D.

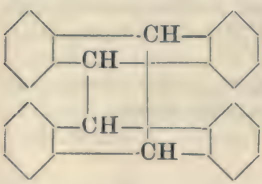
The Formula of Organo-magnesium Derivatives: Magnesium Hydride. PIERRE JOLIBOIS (*Compt. rend.*, 1912, 155, 353—355).—For various reasons the author considers that Grignard's formula, EtMgI, for his reagent must be abandoned in favour of the formula $MgEt_2,MgI_2$. If a concentrated solution of the Grignard reagent is submitted to the action of an electric current, with a high potential difference, for a short time until the liquid becomes hot, magnesium is deposited at the cathode, but no gas can be detected at the anode. On heating the reagent gradually by electrical means, under reduced pressure, so that the gaseous products are withdrawn without being able to react on the solid products, the ether is first completely eliminated at 95°, this stage in the reaction being reversible. At 175° an irreversible reaction occurs, almost pure ethylene being evolved to the extent of two molecules for every atom of magnesium. The solid residue at this stage is a grey powder, which must be represented either as HMgI or MgH_2. From it practically all the iodine can be removed by washing with dry ether, and on heating it to 280° it evolves hydrogen to the extent of one molecule per atom of magnesium. The author considers that these results support his formula $MgEt_2,MgI_2$.

W. G.

Preparation of Carboxylic Acid Esters Containing Mercury and the Products of their Hydrolysis. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 246207).—Complex mercury salts of unsaturated carboxylic acids have previously been prepared (this vol., i, 596); it is now found that similar compounds can be obtained from the mono- and poly-carboxylic acids of the acetylene series which are of therapeutic value.

An alcoholic solution of mercuric acetate when treated with an equal weight of ethyl behenolate and allowed to remain at the ordinary temperature during twenty-four hours furnishes a *product* which, after hydrolysis with cold sodium hydroxide, contains about 35% mercury. The analogous compound from ethyl stearolate contains 30% of mercury. F. M. G. M.

1-Methylanthracene and Some Anthracene Derivatives. OTTO FISCHER and HUGO ZIEGLER (*J. pr. Chem.*, 1912, [ii], 86, 289—297).—A continuation of previous work on 1-methylanthracene (Abstr., 1911, i, 279), together with an account of the polymerisation of a number of anthracene derivatives by exposure to sunlight in benzene solution. It is found that dihydroanthracene, methyldihydroanthracene, and anthraquinone, which do not contain a para-linkage, undergo no change, whereas 1-methylanthracene, 1-chloro-4-methylanthracene, 9-bromoanthracene, and 1-chloro-9(or 10)-bromoanthracene, in which the para-bond remains intact, readily polymerise to dianthracenes. From these observations the conclusion is drawn that the polymerisation is due to the rupture of the para-linking, followed by the union of two molecules as shown in the annexed formula. Further, since the dianthracenes do not combine with picric acid, the basic properties of anthracene derivatives, and also their halochromism, must be referred to the presence of the para-bond.



1-*Methyl*-9 : 10-*dihydroanthracene*, prepared by reducing 1-methylanthracene with sodium and amyl alcohol, distils at 314—315°/740 mm., and solidifies in colourless, transparent needles, m. p. 30°.

1-Chloro-4-methylanthracene forms a *picrate*, crystallising in dark red needles, m. p. 118°, and combines with bromine in carbon disulphide solution, yielding 1-*chloro*-9 : 10-*dibromoathracene*, pale green prisms (decomp. 139°). On treatment with hydrogen iodide in glacial acetic acid solution, it is reduced to 1-*chloro*-4-*methyl*-9 : 10-*dihydroanthracene*, which crystallises in long, white needles, m. p. 47—48°, gives blue fluorescent solutions, and dissolves in strong sulphuric acid with a reddish-yellow coloration.

1-*Chloro*-4-*methylanthranol*, prepared by passing hydrogen iodide into a boiling solution of 1-chloro-4-methylanthraquinone in glacial acetic acid solution, forms long, light yellow needles, m. p. 145—146°.

When gently warmed with strong nitric acid, 1-methoxy-4-methylanthraquinone is converted into *nitro*-1-*hydroxy*-4-*methylanthraquinone*,

$C_{15}H_9O_5N$, which crystallises in lustrous, orange prisms, m. p. 182°, and dissolves in aqueous alkalis, yielding reddish-violet salts.

Nitro-1-*methylanthraquinone*, prepared by nitrating 1-methylanthraquinone with strong nitric acid, forms lustrous, light yellow needles, m. p. 252°, and is oxidised by dilute nitric acid at 200° to *nitroanthraquinone*-4-*carboxylic acid*, crystallising in stellar aggregates of brownish-yellow needles (decomp. 270°).

1-Chloroanthraquinone is reduced by zinc dust and strong aqueous ammonia to 1-*chloroanthracene*. This forms white leaflets, m. p. 79°, yields a *picrate*, crystallising in red needles, m. p. 101—102°, and combines with bromine (1 mol.) in carbon disulphide solution to form an unstable *additive* compound, which rapidly loses hydrogen bromide, yielding 1-*chloro*-9(or 10)-*bromoanthracene*. The latter compound crystallises in long, slender, sulphur-yellow needles, m. p. 143—144°.

Bis-1-*methylanthracene*, prepared by exposing a benzene solution of 1-methylanthracene to direct sunlight for three to four days, crystallises in lustrous, colourless plates containing benzene, which is lost on exposing the crystals in air; it has m. p. 246°, and on distillation is reconverted into 1-methylanthracene.

Bis-1-*chloroanthracene*, obtained in a similar manner, forms white, well-developed crystals of a rhombic habit, m. p. 235°.

Bis-1-*chloro*-4-*methylanthracene* separates in stout, white, efflorescent crystals, m. p. 231°, containing benzene.

Bis-9-*bromoanthracene* crystallises in clusters of greenish-yellow needles, m. p. 274°.

Bis-1-*chloro*-9(or 10)-*bromoanthracene* forms stout, white prisms, m. p. 220°. F. B.

Additive Products of Trinitrobenzene: Derivatives with Certain Aromatic Nitrogen Compounds. Roberto Ciusa and L. Vecchiotti (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 161—166).—The following *additive* compounds have been obtained by interaction of the components, either alone or in boiling alcoholic solution:

2-Methylindole and *s*-trinitrobenzene, $C_9H_9N,C_6H_3(NO_2)_3$, red needles, m. p. 152° (compare Sudborough and Beard, Trans., 1910, 97, 773). 2-Methylindole and trinitrotoluene, $C_9H_9N,C_6H_2Me(NO_2)_3$, yellow needles, m. p. 110°. 2-Methylindole and trinitroaniline, brick-red needles showing metallic lustre, m. p. 166°. 2-Methylindole and picryl chloride, $C_9H_9N,C_6H_2Cl(NO_2)_3$, red needles, m.p. 115°. 3-Methylindole and picryl chloride, red needles, m. p. 120° (compare Ciusa and Agostinelli, Abstr., 1907, i, 553). 2:3-Dimethylindole and *s*-trinitrobenzene, $C_{10}H_{11}N,C_6H_3(NO_2)_3$, red needles, m. p. 175°. 2:3-Dimethylindole and trinitrotoluene, $C_{10}H_{11}N,C_6H_2Me(NO_2)_3$, red needles, m. p. 118°. 2:3-Dimethylindole and picryl chloride, $C_{10}H_{11}N,C_6H_2Cl(NO_2)_3$, dark red needles, m. p. 140°. Tetrahydrocarbazole and picryl chloride, chocolate-brown needles, m. p. 121°. Carbazole and trinitrotoluene give two compounds: (1) $2C_{12}H_9N,3C_6H_2Me(NO_2)_3$, yellow needles, m. p. 160°, and (2) $C_{12}H_9N,C_6H_2Me(NO_2)_3$, dark yellow needles, melting at 140—200°. Carbazole and picryl chloride,

$$C_{12}H_9N,C_6H_2Cl(NO_2)_3,$$

dark red crystals softening at 140°, m. p. 155°. Phenylindole and trinitrotoluene, $2C_{14}H_{11}N,3C_6H_2Me(NO_2)_3$, yellow needles, m. p. 97°. Phenylindole and picryl chloride, $C_{14}H_{11}N,C_6H_2Cl(NO_2)_3$, carmine-red needles, m. p. 119°. T. H. P.

Morphological Studies of Benzene Derivatives. III. *p*-Dibromobenzenesulphonates (Isomorphous) of the "Rare Earth" Elements—a means of Determining the Directions of Valency in Tervalent Elements. HENRY E. ARMSTRONG and ERNEST H. RODD (*Proc. Roy. Soc.*, 1912, *A*, **87**, 204—217. Compare Trans., 1910, **97**, 1578; Colgate and Rodd, *ibid.*, 1585).—Lanthanum, neodymium, praseodymium, and cerium form *p*-dibromobenzenesulphonates, which crystallise from water at the ordinary temperature with 18 molecules of water. The crystals are monoclinic, and the four salts appear to be isomorphous. At about 35° they are converted into salts containing 9 molecules of water, which crystallise in well-formed rhombic prisms. In the case of samarium, the higher hydrate only has been obtained, but this also appears to be isomorphous with the corresponding salts of the other four metals. The gadolinium salt crystallises with 12 and 7 molecules of water. Both hydrates crystallise out from solution at 37°, but at 50° the lower hydrate only is obtained. These observations indicate that, as the atomic weight of the metal increases, peculiarities are exhibited which are not evident in the case of the lower members of the series.

Crystallographic data for the four salts represented by

$$M(C_6H_3Br_2{\cdot}SO_3)_3,9H_2O$$

are recorded, and these show that the salts are closely isomorphous, the approximation of the neodymium, praseodymium, and lanthanum salts being much closer than that ordinarily observed between members of an orthorhombic isomorphous series. The pseudotrigonal character of the salts indicates that the crystal structure is derived from the benzene structure of cubic origin typified by *p*-di-iodobenzene, and by reference to the values of the axial ratios, it is shown that the relationships required by theory are satisfied in a quantitative manner. This quantitative correspondence between the crystal structure of *p*-di-iodobenzene and the rare earth salts described affords strong evidence of the correlation of crystalline form with chemical composition and constitution.

The agreement in question shows, further, that the valency directions of the tervalent elements of the rare earth series are symmetrically disposed, the metal occupying the central position in a plane containing three benzene groups. A new method is thus indicated by means of which, the directions in which valency acts, may be determined.

H. M. D.

Preparation of ω-2-Dinitrotoluene, its Homologues and Derivatives. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 246381. Compare this vol., i, 176).—When *o*-nitrotoluene (2000 parts) is heated at 130—140° during three hours with the vapour of nitric acid (1000 parts) it yields 400—500 parts of ω-2-dinitrotoluene.

F. M. G. M.

Migration of the Nitro-group. GIACOMO PONZIO (*Gazzetta*, 1912, 42, ii, 55—57).—When treated with benzenediazonium chloride, 9-nitrofluorene, which is capable of giving salts corresponding with the formula: $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>C{:}NO_2H$, yields an unstable product,

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>C<\begin{matrix} NO_2 \\ N_2Ph \end{matrix},$$

which undergoes intramolecular rearrangement with formation of fluorenone-*p*-nitrophenylhydrazone, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>C{:}N_2H{\cdot}C_6H_4{\cdot}NO_2$. This behaviour of 9-nitrofluorene is similar to that previously observed with ω-dinitrotoluene, ω-nitrophenylacetonitrile, and ω-nitrodiphenylmethane (Abstr., 1910, i, 192, 194; this vol., i, 547). T. H. P.

Preparation of Four Di*cyclo*hexylpropanes. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1912, 155, 385—388. Compare this vol., i, 617).—The authors have applied their method of direct hydrogenation to the preparation of di*cyclo*hexylpropanes.

αγ-Di*cyclo*hexylpropane, D_0^0 0·8874, D_0^{21} 0·8701, n_D 1·475, b. p. 289—290° (corr.), was obtained by direct hydrogenation with nickel at 175° of dibenzyl ketone, the latter being prepared by catalysis of phenylacetic acid over thoria at 400° (compare Frézouls, this vol., i, 629).

αβ-Di*cyclo*hexylpropane, D_0^0 0·8891, D_0^{21} 0·8725, n_D 1·479, b. p. 272—273° (corr.), was prepared from phenylbenzylmethylcarbinol, b. p. 289—292°, as a starting point, by dehydrating this over thoria at 300°, and reducing the αβ-diphenylpropylene thus formed (Klages, Abstr., 1902, i, 668) to αβ-diphenylpropane, D^{23} 0·9745, n_D 1·455, b. p. 280—282° (corr.), and this in turn to the substance required.

Diphenylethylcarbinol, $HO{\cdot}CPh_2{\cdot}Et$, m. p. 95° (Masson, Abstr., 1903, i, 28), on distillation yields (1) αα-diphenyl-Δ^{α}-propylene, D^{23} 1·0076, n_D 1·593, m. p. 51·5°, b. p. 284·5° (corr.), which separates from alcohol in pearly leaflets, and (2) a small amount of *αα-diphenyl-Δ^{β}-propylene*, D^{24} 1·0038, n_D 1·587, b. p. 279—281° (corr.), which is liquid. These two isomerides on direct hydrogenation over partly spent nickel yield the same αα-diphenylpropane, D_0^{24} 0·9881, n_D 1·569 (Klages and Heilmann, Abstr., 1904, i, 487). This on being passed twice over nickel at 175° is quantitatively converted into *αα-di*cyclo*hexylpropane*, D_0^0 0·9038, D_0^{23} 0·8887, n_D 1·485, b. p. 270—271° (corr.).

ββ-Diphenylpropane (Silva, Abstr., 1880, 259), D_0^{25} 0·9958, n_D 1·570, m. p. 29°, b. p. 282—283° (corr.), prepared by Friedel and Craft's method is reduced, with some decomposition, by nickel at 175°, yielding *ββ-di*cyclo*hexylpropane*, D_0^0 0·9158, D_0^{23} 0·9002, n_D 1·490, b. p. 273—274° (corr.). T. A. H.

Decomposition of Pyrazoline Bases as a means of Obtaining Derivatives of *cyclo*Propane. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 849—865. Compare Abstr., 1911, i, 1028; this vol., i, 245).—The action of hydrazine on camphorone yields a pyrazoline base which, when distilled with alkali, decomposes into a bicyclic hydrocarbon, C_9H_{16}, containing a *cyclo*propane ring. These trans-

formations are completely analogous to those occurring with mesityl oxide and pulegone.

The *pyrazoline base*, $CH_2<\begin{matrix}CH_2\text{—}CH\cdot CMe_2\\ CHMe\cdot C\text{===}N\end{matrix}>NH$, has b. p. 119—120°/37 mm., D_0^{20} 0·9515, n_D 1·4759, and is transformed into pulegenone when boiled with hydrochloric acid.

2 : 6 : 6-*Trimethyl*-0 : 1 : 3-bicyclo*hexane*, $CMe_2<\begin{matrix}CH\cdot CHMe\\ CH\text{—}CH_2\end{matrix}>CH_2$, obtained by distilling the pyrazoline base with potassium hydroxide and platinised porcelain, has b. p. 140·5°/752 mm., $D_0^{18\cdot5}$ 0·8229, D_0^{20} 0·8223, $n_D^{18\cdot5}$ 1·4465, and resembles light petroleum in odour. When reduced by Sabatier and Senderens' method, it yields 1 : 1 : 3-trimethyl*cyclo*hexane. By the action of hydrogen bromide, this bicyclic hydrocarbon is converted into the bromo*cyclo*pentane derivative,

$$CMe_2Br\cdot CH<\begin{matrix}CH_2\text{—}CH_2\\ CHMe\cdot CH_2\end{matrix},$$

which loses the elements of hydrogen bromide in two ways: (1) the action of alcoholic potassium hydroxide gives 1-*methyl*-2-iso*propylidene*-cyclo*pentane*, $CMe_2{:}C<\begin{matrix}CH_2\text{—}CH_2\\ CHMe\cdot CH_2\end{matrix}$, b. p. 149—151°/755 mm., D_0^{20} 0·8104, n_D 1·4518, which forms an orange coloration with sulphuric acid in acetic acid solution, yields a blue, oily nitrosochloride, and gives acetone and 1-methyl*cyclo*pentanone when oxidised with permanganate; (2) distillation with aniline yields, in addition to 1-methyl-2-*iso*-propylidene*cyclo*pentane, 1-*methyl*-2-iso*propenyl*cyclo*pentane*, $CH_2{:}CMe\cdot CH<\begin{matrix}CHMe\cdot CH_2\\ CH_2\text{—}CH_2\end{matrix}$, b. p. 141—143°/757 mm., D_0^{20} 0·8006, n_D 1·4455. These two hydrocarbons are interconvertible, (1) into (2) partly by addition of hydrogen bromide and its removal by means of aniline, and (2) into (1) completely by addition of hydrogen bromide and treatment with alcoholic potassium hydroxide. Reduction of either hydrocarbon by Sabatier and Senderens' method yields 1-*methyl*-2-iso*propyl*cyclo*pentane*, $\begin{matrix}CHMe\cdot CH_2\\ CHPr^{\beta}\cdot CH_2\end{matrix}>CH_2$, b. p. 142·5°/759 mm. D_0^{15} 0·7833, D_0^{20} 0·7792, n_D^{20} 1·4279.

The interaction of styryl methyl ketone and hydrazine gives 5-*phenyl-3-methylpyrazoline*, $\begin{matrix}NH\cdot CHPh\\ N\text{==}CMe\end{matrix}>CH_2$, which is a colourless liquid, b. p. 180°/32 mm., D_0^{20} 1·0669, n_D 1·5956; its *hydrochloride*, $C_{10}H_{12}N_2,HCl$, was prepared. When heated with potassium hydroxide and platinised porcelain, the pyrazoline base is converted into 2-*phenyl*-1-*methyl*cyclo*propane*, $\begin{matrix}CHMe\\ CHPh\end{matrix}>CH_2$, b. p. 186°/743 mm., 186·3°/747 mm., 186·5°/749 mm., D_0^{20} 0·9198, n_D 1·5208. The action of hydrobromic acid on this hydrocarbon gives *a-bromo*iso*butylbenzene*, $C_6H_5\cdot CHBr\cdot CHMe_2$, a colourless liquid, b. p. 135—137°/37 mm., D_0^{20} 1·2609, n_D 1·5414, and this, when distilled with quinoline, yields *iso*butenylbenzene, the nitrosite of which has m. p. 122°.

T. H. P.

Preparation of ***p*****-Nitroacetoacetanilide.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 246382).—p-*Nitroacetoacetanilide*, yellow leaflets, m. p. 124°, crystallising from water, is prepared by dissolving acetoacetanilide (177 grams) in 350 c.c. of concentrated sulphuric acid at 0°, slowly adding 250 grams of nitric acid, and meanwhile maintaining the temperature below 3°; on reduction it furnishes p-*aminoacetoacetanilide*. F. M. G. M.

Decomposition of Diphenylnitrosoamine by Heat. MARQUEYROL and D. FLORENTIN (*Bull. Soc. chim.*, 1912, [iv], 11, 804—805).—The authors confirm Wieland's observation (Abstr., 1911, i, 569) that diphenylnitrosoamine is decomposed by heat, giving a quantitative yield of nitric oxide. The decomposition takes place at 40° under reduced pressure, but soon slackens unless the nitric oxide is removed as it forms. Heating the nitrosoamine in an oil-bath at 180—190° is a convenient method of preparing nearly pure nitric oxide. T. A. H.

Preparation of Organic Compounds containing Sulphur. KNOLL & Co. (D.R.-P. 247186).—The compounds obtained by fusing organic substances with sulphur are (with the exception of diphenylamine derivatives) obtained in a more satisfactory manner if the operation is carried out in the presence of iodine.

The following *compounds* have been prepared (1) from equal parts of sulphur and phenanthraquinone at 240—260° with about 1% of iodine; (2) the same with anthraquinone; and (3) with quinizarin.

(4) From aminoanthraquinone (1 part), sulphur (3 parts) and 1% of iodine at 260°.

(5) β-Naphthylamine (286 parts), sulphur (64 parts), with 1—2% of iodine at 200° during two and a-half hours, furnished a quantitative yield of *thio-ββ-dinaphthylamine*, m. p. 236°.

(6) α-Naphthylamine (143 parts), aniline (93 parts), sulphur (32 parts), with 1—2% of iodine at 200° yielded *thiophenyl-α-naphthylamine*, m. p. 137°, whilst (7) β-naphthol under the same conditions furnished *thiophenyl-β-naphthylamine*, m. p. 176°. F. M. G. M.

α-Phenyl-mono- and -di-benzylethylamines. KNUT PARCK (*J. pr. Chem.*, 1912, [ii], 86, 284—288).—*α-Phenyl*-N-*benzylethylamine*, $CHMePh\cdot NH\cdot C_7H_7$, obtained in the form of its *hydrochloride*, short prisms, m. p. 184°, by heating molecular proportions of α-phenylethylamine and benzyl chloride on the water-bath, is a colourless liquid, b. p. 171°/15 mm., D^{20} 1·009, and forms a *nitrate*, lustrous, silky needles, m. p. 124°, a *hydrogen sulphate*, $C_{15}H_{17}N,H_2SO_4$, m. p. 166°, and a *hydrogen oxalate*, crystallising in small plates, m. p. 193°; the *acetate* and *hydrogen racemate* are also mentioned.

It is accompanied by a small amount of *α-phenyl*-N-*dibenzylethylamine*, $CHMePh\cdot N(C_7H_7)_2$, which forms long, slender needles, m. p. 58°, and yields a *hydrochloride*, crystallising in small plates, m. p. 196°.

The resolution of the monobenzyl compound into its optically active components has been accomplished by the crystallisation of its hydrogen *d*-tartrate from water.

The *hydrogen* d-*tartrate* of the *l*-base, $C_{19}H_{23}O_6N,3H_2O$, is the less soluble, and separates in long, efflorescent prisms, m. p. 72°, from which l-*a-phenyl*-N-*benzylethylamine* is obtained, having b. p. 171°/15 mm., and $[\alpha]_D^{20}$ −39·7°.

The optically active monobenzyl compounds are most readily prepared by heating the active α-phenylethylamines with benzyl chloride, small amounts of the active α-phenyldibenzylethylamines being produced simultaneously; thus *d*-α-phenylethylamine is converted into d-*a-phenyl*-N-*benzylethylamine*, which has $[\alpha]_D^{20}$ +39·9°. The salts of the active monobenzyl compounds resemble those of the inactive base; the *hydrochloride* has m. p. 177°; the *nitrate*, m. p. 113°. The *hydrogen* d-*tartrate* of the *d*-base crystallises with $2H_2O$ in triangular plates, m. p. 62°.

l-*a-Phenyl*-NN-*dibenzylethylamine* has $[\alpha]_D^{20}$ − 97·7° in alcoholic solution; the d-*isomeride*, $[\alpha]_D^{20}$ +99·3°; both forms have m. p. 74°, and yield *hydrochlorides*, m. p. 197°. F. B.

Action of Tribromophenol and *p*-Bromophenol on Toluene in the Presence of Aluminium Chloride. MORITZ KOHN and FRIEDRICH BUM (*Monatsh.*, 1912, **32**, 923—928).—It has already been shown (Kohn and Müller, Abstr., 1909, i, 567) that in the action of tribromophenol on benzene in the presence of aluminium chloride a transference of bromine occurs from the tribromophenol to the hydrocarbon producing phenol and bromobenzene.

The interaction of tribromophenol, toluene, and aluminium chloride on the water-bath produces phenol and *m*-bromotoluene, the identity of which was proved by oxidation to *m*-bromobenzoic acid. At higher temperatures (130—140°) a fair amount of phenol is still obtained, but the yield of bromotoluene is meagre, much resinous matter being formed.

If in the above reaction the tribromophenol is replaced by *p*-bromophenol, *m*-bromotoluene and phenol are obtained. D. F. T.

Preparation of Neutral Phosphoric Acid Esters of Phenols and Naphthols with Their Homologues and Derivatives. ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 246871. Compare Abstr., 1883, 1108; 1894, i, 578).—The neutral esters of phosphoric acid can be obtained in quantitative yield when anhydrous alkali phenoxides or naphthoxides are treated with phosphoryl chloride in the presence of an indifferent anhydrous solvent. The following compounds are described: the tri-*o*-tolyl ester; the tri-α-naphthyl ester, m. p. 148—149° (Autenrieth, Abstr., 1898, i, 14, gives 145°); the triphenyl ester; the tri-*p*-chlorophenyl ester, m. p. 112° (*loc. cit.*, gives 99—100°), and the tri-1-chloro-2-naphthyl ester. F. M. G. M.

Bromo- and Chloro-guaiacols. TEMISTOCLE JONA (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 202—208).—5-Bromoguaiacol,

$$OH\cdot C_6H_3Br\cdot OMe\ [OH:OMe:Br = 1:2:5],$$

obtained from 5-aminoguaiacol (Jona and Pozzi, Abstr., 1911, i, 854), forms white crystals, m. p. 62—65°, and gives a bluish-green coloration with ferric chloride. 5-*Bromo*-1-*benzoylguaiacol*, $C_{14}H_{11}O_3Br$, forms

white needles, m. p. 73—75°. 5-*Bromo*-1-*acetylguaiacol*, $C_9H_9O_3Br$, separates in white leaflets, m. p. 63—65°. 5-*Bromoguaiacol ethyl ether*, $C_9H_{11}O_2Br$, crystallises in slender, white needles, m. p. 58—60·5°. 5-*Bromoveratrole*, $C_8H_9O_2Br$, forms a straw-yellow liquid, heavier than water, b. p. 239—242°/55 mm. 5-*Bromo*-1-*ethylcarbonatoguaiacol*,

$C_{10}H_{11}O_4Br$,

crystallises in slender, silky needles, m. p. 46—49°. *o*-Nitrovanillic acid, identical with that obtained by Tiemann and Matsmoto (Abstr., 1876, ii, 524), may be prepared, along with several other products not yet investigated, by oxidising *o*-nitrovanillin (compare Pschorr and Sumuleanu, Abstr., 1900, i, 178). 3-*Aminoguaiacol*, $C_7H_9O_2N$, obtained by reducing *o*-nitrovanillic acid, forms straw-yellow needles, m. p. 97—100°, and 3-*acetaminoguaiacol*, $C_9H_{11}O_3N$, white crystals, m. p. 120—122°. 3-*Chloroguaiacol*, $C_7H_7O_2Cl$, forms white leaflets, m. p. 31·5—33°, and, in aqueous alcoholic solution, gives a greenish coloration with ferric chloride. 3-*Chloro*-1-*benzoylguaiacol*, $C_{14}H_{11}O_3Cl$, forms white needles, m. p. 36·5—38°, whilst 3-*chloro*-1-*acetylguaiacol*, $C_9H_9O_3Cl$, is a colourless liquid, b. p. 179—181°/55 mm. (corr.). 3-*Chloroguaiacol ethyl ether*, $C_9H_{11}O_2Cl$, is a colourless liquid, b. p. 162—165°/55 mm. (corr.). T. H. P.

Aceteins of Phenol. Ettore Vassallo (*Gazzetta*, 1912, **42**, ii, 237—243).—Condensation of phenol with acetic anhydride in presence of sulphuric acid yields a product different from that obtained by Rasinski (Abstr., 1882, 1288) in presence of zinc chloride, namely, *diphenoxymethylcarbinol*, $OH\cdot CMe(OPh)_2$, which forms a red, flocculent precipitate, m. p. about 228—232°. The same compound is obtained, but in diminished yield, when acetic acid is used in place of the anhydride. It acts as an indicator and yields the *acetyl* derivative, $C_{14}H_{13}O_3\cdot OAc$, m. p. about 133°.

The mechanism of the action of acetic anhydride on phenol is quite comparable with that of phthalic anhydride (compare Oddo and Vassallo, this vol., i, 792). The only difference is that, with open-chain anhydrides, the acid generated separates and the carbinol function of the molecule is preserved, whilst with cyclic anhydrides the carboxyl and hydroxyl, becoming united to the same molecule at a favourable distance apart, react to form a closed lactonic ring. T. H. P.

Di-*p*-hydroxydiphenyl*iso*pentane. A. Ivanoff (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 907—909).—*Di*-p-*hydroxydiphenyl*iso*pentane*, $CHMe_2\cdot CH_2\cdot CH(C_6H_4\cdot OH)_2$, prepared by the condensation of phenol with *iso*valeraldehyde (compare Lunjak, Abstr., 1908, i, 416) in presence of a small proportion of hydrochloric acid, crystallises in needles, m. p. 154°. The *dibenzoyl* derivative, $C_{31}H_{28}O_4$, m. p. 146°, and the *dimethyl* ether, $C_{19}H_{24}O_2$, b. p. 230—230·5°/11 mm., D_0^0 1·0629, D_{20}^{20} 1·0506, D_4^0 1·0627, D_4^{20} 1·0487, were prepared; oxidation of the latter compound by means of chromium trioxide yields the dimethyl ether of di-*p*-hydroxybenzophenone and anisic acid. T. H. P.

Two Forms of Decahydro-β-naphthol: Peculiar Case of Stereoisomerism. Luigi Mascarelli and Giacomo Recusani (*Gazzetta*, 1912, **42**, ii, 35—41).—For decahydro-β-naphthol, Leroux

(Abstr., 1905, i, 278) gave m. p. 75° and b. p. 238°, whilst Ipatieff (*Ber.*, 1907, 40, 1281) gave m. p. 99—100° and b. p. 242—244°.

On purifying a specimen of the compound supplied to them by Ipatieff, the authors found it to consist of a mixture of the two forms, which possess similar properties and are evidently the racemic modifications corresponding with two pairs of optical isomerides. The complete hydrogenation of β-naphthol renders the carbon atoms in the 2-, 9-, and 10-positions asymmetric, and as the last two of these form part of two different nuclei, theory would indicate the possible existence of two pairs of enantiomorphous compounds (compare Piccinini, Abstr., 1900, i, 249; Aschan, Abstr., 1901, i, 477, and Skraup, Abstr., 1903, ii, 67). T. H. P.

Phenyldesoxyn of Dextrose. ALEXANDER M. NASTUKOFF and I. I. KOTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1152—1163. Compare Abstr., 1907, i, 413).—Oxidation of the β-phenyldesoxyn of dextrose in glacial acetic acid solution by means of nitric acid yields 50% of a bright yellow, insoluble nitro-product, which was not examined further, together with *o*-nitrobenzoic and 3:5- and 2:4-dinitrobenzoic acids.

When reduced with zinc and acetic acid, the β-phenyldesoxyn yields a product which agrees in elementary composition and chemical properties with the original compound, but is of a purer yellow colour and contains no sulphur. In order to distinguish this product from the sulphur-free β-phenyldesoxyn (Abstr., 1907, i, 413), the authors term it simply desoxyn.

Two formulæ are suggested for desoxyn: (1) $C_6H_7O_2Ph_3$, representing the anhydride of dextrose, in which three hydroxyl groups are replaced by phenyl groups; this is termed the "hydroxylic" formula. (2) $C_6H_6O_2Ph_2$ or

$$\cdot CPh_2\cdot \overset{O}{\overbrace{CH—CH}}\cdot \overset{O}{\overbrace{CH—CH}}\cdot CH_2\cdot,$$

according to which the formation of desoxyn would be represented by the equation: $C_6H_{10}O_5 + 2C_6H_6 - 3H_2O = C_{18}H_{16}O_2$; this formula is termed the "ketonic." The results of analysis of phenyldesoxyn and also the proportion of benzoic acid formed on oxidation with permanganate indicate the ketonic formula to be the more probable. Determinations of the molecular weight of phenyldesoxyn in freezing phenol and in boiling chloroform give unsatisfactory results, the values obtained varying almost proportionally with the concentration.

The principal soluble product formed simultaneously with phenyldesoxyn is found to be benzenesulphonic acid.

When phenyldesoxyn is subjected to prolonged shaking with concentrated sulphuric acid, it is converted into a product soluble in water. This is termed sulphodesoxynic acid of dextrose, and its formula is either $(C_6H_7O_2)_2(C_6H_5)_3(C_6H_4\cdot SO_3H)_3$ or

$$(C_6H_5\cdot C_6H_6O_2\cdot C_6H_4\cdot SO_3H)_3,$$

the latter appearing to be the more probable. T. H. P.

Sulphur Aryl Chlorides [Aryl Chlorothiols]. THEODOR ZINCKE (*Annalen*, 1912, 391, 55—56).—The term sulphur aryl chloride is

used by the author to denote substances of the type ArSCl [aryl chlorothiols]. Such are produced by the action of chlorine on aromatic mercaptans or their disulphides. They are also obtained by the chlorination of aryl benzyl sulphides, the benzyl group being eliminated in the form of benzylidene chloride.

The corresponding hydroxides, ArS·OH, have not been obtained, but anhydrides, ArS·O·SAr, and esters, ArS·OR, have been prepared.

C. S.

Sulphur *o*-Nitrophenyl Chloride [*o*-Nitrochlorothiolbenzene] and its Transformation Products. THEODOR ZINCKE and FR. FARR (*Annalen*, 1912, 391, 57—88).—o-*Nitrochlorothiolbenzene*,

$NO_2 \cdot C_6H_4 \cdot SCl$,

m. p. 75°, yellow needles, is readily obtained in more than 90% yield by repeatedly saturating a suspension of finely divided *oo'*-dinitrodiphenyl disulphide in carbon tetrachloride with chlorine in the absence of moisture, until the disulphide has disappeared. The substance is stable and extremely reactive, behaving like an acid chloride in some cases, and like a diazo-compound towards phenols and some aromatic amines. In hot glacial acetic acid, it is converted by nitric acid (D 1·4) into a mixture of *o*-nitrobenzenesulphonic acid and its chloride. Methyl or ethyl alcohol in the cold converts the substance into *oo'*-dinitrodiphenyl disulphide and *oo'*-dinitrodiphenyl disulphoxide, and at the b. p. into the disulphide and the sulphinic acid. When boiled with dilute methyl alcohol, *o*-nitrochlorothiolbenzene undergoes complicated changes, and yields the disulphide, the sulphinic acid, *o*-nitrobenzenesulphonic acid, and aniline-*o*-sulphonic acid. In glacial acetic acid, *o*-nitrochlorothiolbenzene is converted into *o*-nitrophenyl thiocyanate by potassium cyanide.

o-*Nitrobromothiolbenzene*, $NO_2 \cdot C_6H_4 \cdot SBr$, m. p. 85°, obtained in a similar manner as the chloro-derivative, forms long, golden needles.

o-*Nitrothiophenyl oxide*, $O(S \cdot C_6H_4 \cdot NO_2)_2$, prepared by shaking *o*-nitrochlorothiolbenzene with water for several hours, crystallises in yellow plates, blackens at 92—93°, and explodes; in a capillary tube, explosion does not occur, the blackening at 92—93° being followed by fusion above 180°. The oxide is reconverted into *o*-nitrochlorothiolbenzene by concentrated hydrochloric acid or phosphorus pentachloride. It dissolves in alkalis or aqueous ammonia with a deep blue colour (probably due to a salt of the hydroxide, $NO_2 \cdot C_6H_4 \cdot S \cdot OH$); the colour soon disappears, and the disulphide and the sulphinic acid are obtained.

Esters of *o*-nitrophenylsulphinous acid, $NO_2 \cdot C_6H_4 \cdot S \cdot OR$, are obtained by treating a cold alcoholic or ethereal solution of *o*-nitrochlorothiolbenzene with the sodium alkyloxide. They are reconverted into the chloride by concentrated hydrochloric acid, and are decomposed by alkalis, yielding the disulphide and the disulphoxide. The *methyl* ester, m. p. 54°, yellow plates or needles; *ethyl* ester, m. p. 26°, yellow needles, and *phenyl* ester, m. p. 72°, yellow plates or needles, are described.

oo'-*Dinitrodiphenyl disulphoxide*, $O_2S_2(C_6H_4 \cdot NO_2)_2$, m. p. 142—143°, colourless leaflets, is obtained, together with the disulphide, by decom-

posing *o*-nitrochlorothiolbenzene by methyl or ethyl alcohol, alkalis, potassium or sodium acetate, or moist silver oxide. o-*Nitrophenylsulphinic acid*, $NO_2\cdot C_6H_4\cdot SO_2H$, m. p. 124° (*methyl* ester, m. p. 106°; *ethyl* ester, m. p. 107°), is described.

In ethereal solution, *o*-nitrochlorothiolbenzene behaves like an acid chloride towards ammonia, methylamine, dimethylamine, aniline, and *p*-toluidine, yielding substances called *thiolamines*. o-*Nitrophenylthiolamine*, $NO_2\cdot C_6H_4\cdot S\cdot NH_2$, m. p. 124—125° (decomp.), yellow needles, behaves in many ways like a primary aromatic amine. It cannot be diazotised, but forms an *acetyl* compound, yellow crystals, m. p. 179°, blackening at 173—175°, *benzylidene* derivative, m. p. 159°, yellow needles, and iso*propylidene* derivative, $NO_2\cdot C_6H_4\cdot S\cdot N\colon CMe_2$, yellow needles, m. p. 86°, stable to alkalis; it yields the disulphide and ammonium iodide when heated with methyl iodide, is reconverted into *o*-nitrochlorothiolbenzene by concentrated hydrochloric acid, and is converted by boiling dilute hydrochloric or acetic acid into oo'-*dinitrodiphenyldithiolimine*, $NH(S\cdot C_6H_4\cdot NO_2)_2$, m. p. 217° (decomp.), citron-yellow powder or needles. o-*Nitrophenylthiolmethylamine*,

$$NO_2\cdot C_6H_4\cdot S\cdot NHMe,$$

m. p. 36°, forms yellow, glistening needles; the *methylimine*,

$$NMe(S\cdot C_6H_4\cdot NO_2)_2,$$

yellow crystals, has m. p. 204—205° (decomp.). o-*Nitrophenylthioldimethylamine*, $NO_2\cdot C_6H_4\cdot S\cdot NMe_2$, m. p. 63°, forms yellow leaflets or needles. Corresponding *compounds*, $NO_2\cdot C_6H_4\cdot S\cdot NHPh$, m. p. 94°, red crystals, and $NO_2\cdot C_6H_4\cdot S\cdot NH\cdot C_7H_7$, m. p. 133°, yellow leaflets or needles, obtained from aniline and *p*-toluidine respectively, are described.

Towards α- and β-naphthylamines, however, *o*-nitrochlorothiolbenzene behaves like a diazo-chloride, substitution occurring in the naphthalene nucleus. In cold chloroform or ether the reactions are similar to those of the preceding amines, α- and β-*naphthalides*,

$$NO_2\cdot C_6H_4\cdot S\cdot NH\cdot C_{10}H_7,$$

m. p. 129° and 188° respectively, being formed; in boiling acetic acid, however, *o*-nitrochlorothiolbenzene reacts with α-naphthylamine to form 1-*aminonaphthyl* 2:4-*di*-o-*nitrophenyl disulphide*,

$$NH_2\cdot C_{10}H_5(S\cdot C_6H_4\cdot NO_2)_2,$$

m. p. 194°, brownish-red, crystalline powder (*acetyl* compound, m. p. 214—215°), and with β-naphthylamine to form 2-*aminonaphthyl* 1-o-*nitrophenyl sulphide*, $NH_2\cdot C_{10}H_6\cdot S\cdot C_6H_4\cdot NO_2$, m. p. 183—184° (*acetyl* derivative, m. p. 183—184°). The *hydrochlorides* of these two substances can be diazotised, and coupled with β-naphthol to form red dyes. The preceding β-naphthylamine derivative reacts with *o*-nitrochlorothiolbenzene in boiling benzene to form a *compound*,

$$NO_2\cdot C_6H_4\cdot S\cdot C_{10}H_6\cdot NH\cdot S\cdot C_6H_4\cdot NO_2,$$

m. p. 186—187°, yellow, crystalline powder, which is easily decomposed into its generators by glacial acetic and concentrated hydrochloric acids. o-*Nitro*-p'-*dimethylaminodiphenyl sulphide*,

$$NO_2\cdot C_6H_4\cdot S\cdot C_6H_4\cdot NMe_2,$$

m. p. 187—188°, dark red needles, prepared from *o*-nitrochlorothiolbenzene and dimethylaniline in boiling ether, has basic properties; the *hydrochloride* forms canary-yellow needles.

An ethereal solution of *o*-nitrochlorothiolbenzene reacts like a diazo-chloride towards phenols; the hydroxyl group is unattacked, and substitution occurs in the nucleus; thus phenol yields o-*nitro*-p′-*hydroxy-diphenyl sulphide*, $NO_2\cdot C_6H_4\cdot S\cdot C_6H_4\cdot OH$, m. p. 130—131°, yellow crystals (*potassium* salt, reddish-brown needles; *acetyl* derivative, m. p. 81—82°, yellow needles); *a*-naphthol yields o-*nitrophenyl*-1-*hydroxy-naphthyl sulphide*, $NO_2\cdot C_6H_4\cdot S\cdot C_{10}H_6\cdot OH$, m. p. 186°, brick-red crystals (*potassium* salt, reddish-brown leaflets; *acetyl* derivative, m. p. 125—126°, yellow needles); *β*-naphthol yields o-*nitrophenyl*-2-*hydroxy-naphthyl sulphide*, $NO_2\cdot C_6H_4\cdot S\cdot C_{10}H_6\cdot OH$, m. p. 179—180°, yellow needles (*potassium* salt, reddish-brown leaflets; *acetyl* derivative, m. p. 101°, citron-yellow needles); resorcinol yields o-*nitro*-o′p′-*dihydroxy-diphenyl sulphide*, $NO_2\cdot C_6H_4\cdot S\cdot C_6H_3(OH)_2$, m. p. 150—151°, yellow crystals (*acetyl* derivative, m. p. 102—103°, yellow plates). o-*Nitro-phenyl acetonyl sulphide*, $NO_2\cdot C_6H_4\cdot S\cdot CH_2\cdot COMe$, m. p. 81°, obtained from *o*-nitrochlorothiolbenzene and boiling acetone, crystallises in yellow needles or leaflets, and is not decomposed by concentrated hydrochloric or sulphuric acid. C. S.

Oxonium Salts of Some Hydroxyanthraquinone Ethers. OTTO FISCHER and HUGO ZIEGLER (*J. pr. Chem.*, 1912, [ii], 86, 297—305. Compare Abstr., 1911, i, 887).—1:2:5-*Trimethoxyanthra-quinone*, prepared by heating the potassium salt of hydroxyanthrarufin with methyl sulphate at 140°, crystallises in golden-yellow leaflets, m. p. 203—204°. On treatment with hydrogen bromide in benzene solution, it yields an unstable, bluish-green *hydrobromide*; the *zinci-bromide*, $C_{17}H_{14}O_5,HBr,ZnBr_2$, is obtained as a reddish-violet precipitate by passing hydrogen bromide into a suspension of the trimethyl ether in benzene to which a small amount of a saturated solution of zinc bromide in ethyl acetate has been added.

1:2:8-Trimethoxyanthraquinone, obtained in a similar manner from hydroxychrysazin, crystallises in clusters of light yellow needles, m. p. 157°, and forms an unstable reddish-brown, crystalline *hydro-bromide*.

1:4:5:8-Tetrahydroxyanthraquinone crystallises from boiling naphthalene in feather-like aggregates of bronze-coloured needles, and yields solutions having a fiery-red fluorescence; the *tetra-acetyl* derivative crystallises in light yellow needles (decomp. 250°). Its difficultly soluble, blue *potassium* salt yields, with methyl sulphate, 1:4:5:8-*tetramethoxyanthraquinone*, which crystallises in lustrous, orange leaflets, m. p. 317°, and forms a very unstable, bluish-green *hydro-bromide* and a more stable, brownish-black *zincibromide*,

$$C_{18}H_{16}O_6,2HBr,ZnBr_2.$$

[With HANS GROSS.]—When heated with methyl sulphate at 180—190°, the potassium salt of anthrachrysone (1:3:5:7-tetra-hydroxyanthraquinone) yields a *dimethyl ether*, $C_{16}H_{12}O_6$, which crystallises from nitrobenzene in columns of a golden-bronze lustre, and forms a *disodium* salt, long, orange-red needles, and a *diacetyl* derivative, long, citron-yellow needles, m. p. 256°. It is accompanied by a small amount of 1:3:5:7-*tetramethoxyanthraquinone*, crystallising in golden-yellow, flat, lancet-shaped prisms, m. p. 294°. The last-

mentioned compound forms a *perchlorate*, $C_{18}H_{16}O_6,HClO_4$, which forms long, dark red needles, and, on account of its instability, could not be isolated in a pure condition; the unstable, dark red *hydo-bromide* and dark reddish-violet *zincibromide*, $C_{18}H_{16}O_6,HBr,Zn\ r_2$, are also described. F. B.

Synthesis of the 3 : 4 : 5-Trimethoxyphenanthrene obtained from Morphenol. ROLAND PSCHORR (*Annalen*, 1912, **391**, 40—55).—By proving the identity of 3 : 4 : 5-trimethoxyphenanthrene with the trimethyl ether obtained from morphenol, the author has confirmed Vongerichten's constitution of morphenol.

[With F. ZEIDLER and F. DICKHÄUSER.]—m-*Methoxybenzyl alcohol*, b. p. 252°, obtained by the action of concentrated alcoholic potassium hydroxide on *m*-methoxybenzaldehyde, is converted by phosphorus trichloride into m-*methoxybenzyl chloride*, b. p. 124°/13 mm.; the latter is converted through the nitrile into m-*methoxyphenylacetic acid*, m. p. 67°. This acid is obtained more conveniently by heating *m*-methoxybenzaldehyde, hippuric acid, and anhydrous sodium acetate with acetic anhydride; the resulting *lactone* of *α-benzoylamino*-m-*methoxycinnamic acid*, m p. 108°, is boiled with 10% sodium hydroxide, treated with 3% hydrogen peroxide, and acidified, whereby a mixture of *m*-methoxyphenylacetic and benzoic acids is obtained, which is separated by the fractional distillation of their esters under 14 mm. pressure. By condensing sodium *m*-methoxyphenylacetate and 2-nitro-3 : 4-dimethoxybenzaldehyde in acetic anhydride at 100° for three days, 2-*nitro*-3 : 4-*dimethoxy-α*-m-*methoxyphenylcinnamic acid*,

$$NO_2 \cdot C_6H_2(OMe)_2 \cdot CH{:}C(CO_2H) \cdot C_6H_4 \cdot OMe,$$

m. p. 171°, is obtained. The corresponding *amino-acid*, m. p. 153°, obtained by reduction with ferrous sulphate and aqueous ammonia at 93°, is converted by diazotisation and heating into a mixture of 3 : 4 : 5-*trimethoxyphenanthrene*-9-*carboxylic acid*, m. p. 234—235°, prisms, and 3 : 4 : 7-*trimethoxyphenanthrene*-9-*carboxylic acid*, m. p. 214°, long needles, which is separated mechanically. That the former is the chief product is interesting in connexion with the phenomenon of steric hindrance.

[With O. TREIDEL.]—The following compounds have been prepared by reactions similar to the preceding. o-*Nitro-α*-o-*bromophenylcinnamic acid*, obtained from sodium *o*-bromophenylacetate and *o*-nitrobenzaldehyde, has m. p. 163° (corr.). The corresponding *amino-acid* has m. p. 205°. 8-*Bromophenanthrene*-9-*carboxylic acid*, m. p. 295° (corr.), prisms (*ethyl* ester, m. p. 93°), is converted by zinc dust and boiling sodium hydroxide into phenanthrene-9-carboxylic acid.

[With W. KOCH.]—When heated in acetic anhydride, hippuric acid, 6-bromo-3-methoxybenzaldehyde, and sodium acetate yield the *lactone*, m. p. 175°, yellow needles, of 6-bromo-*α*-benzoylamino-3-methoxycinnamic acid. The lactone yields the corresponding *acid*,

$$C_{17}H_{14}O_4NBr,$$

decomp. 223°, by warming with dilute sodium hydroxide and acidifying, but when boiled with 10% sodium hydroxide it is decomposed, yielding benzoic acid, 6-*bromo*-3-*methoxyphenylpyruvic acid*,

$OMe\cdot C_6H_3Br\cdot CH_2\cdot CO\cdot CO_2H$, m. p. 159—160°, ammonia, and p-*bromo*-m-*tolyl methyl ether*, b. p. 108·5°/12 mm. By treating its alkaline solution with 1·5% hydrogen peroxide and acidifying, the substituted pyruvic acid yields 6-*bromo*-3-*methoxyphenylacetic acid*, m. p. 115°. Its sodium salt and 2-nitro-3 : 4-dimethoxybenzaldehyde, condensed in acetic anhydride, yield 2-*nitro*-3 : 4-*dimethoxy*-α-6-*bromo*-3-*methoxyphenylcinnamic acid*,

$$NO_2\cdot C_6H_2(OMe)_2\cdot CH{:}C(CO_2H)\cdot C_6H_3Br\cdot OMe,$$

decomp. 209—211°, which is purified through the *ammonium* salt. The corresponding *amino-acid*, m. p. 200°, yellow leaflets, yields 8-*bromo*-3 : 4 : 5-*trimethoxyphenanthrene*-9-*carboxylic acid*, m. p. 220°, by the usual method. 3 : 4 : 5-Trimethoxyphenanthrene-9-carboxylic acid, m. p. 234°, obtained by the prolonged boiling of an alkaline solution of the preceding acid with alcohol and copper-zinc dust, is heated with glacial acetic acid at 210—220° for forty hours, whereby 3 : 4 : 5-trimethoxyphenanthrene is obtained. Its picrate, m. p. 167°, brownish-red needles with violet reflex, is shown by direct comparison to be identical with a specimen obtained from morphenol. When heated at about 280°/15 mm., 3 : 4 : 5-trimethoxyphenanthrene-9-carboxylic acid is partly converted into methyl 3 : 4 : 5-trimethoxyphenanthrene-9-carboxylate, which is isolated as the *picrate*, m. p. 102°, brick-red needles.

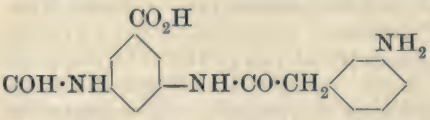
C. S.

Catalytic Preparation of Phenolic and Diphenylene Oxides; Mixed Oxides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1912, **155**, 260—262).—An extension of the study of the catalytic action of thorium oxide on phenols (compare Abstr., 1910, i, 294, 668, 669). By acting on a mixture of phenols, a mixed ether is obtained, together with a certain amount of each simple ether, and in some cases simple or mixed oxides of the type of diphenylene oxide. Mixtures of phenol with each of the three cresols furnish diphenyl ether and the respective tolyl ethers, together with the respective phenyl tolyl ethers, all of which have already been prepared by a different method by Ullmann and Sponagel (compare Abstr., 1907, i, 38). Phenol and α-naphthol yield phenyl ether and phenyl α-naphthyl ether (compare Ullmann and Sponagel, *loc. cit.*). Phenol and β-naphthol yield, in addition to phenyl ether, three distinct crystalline compounds, namely, phenyl β-naphthyl ether, m. p. 46° (compare Ullmann and Sponagel, *loc. cit.*), ββ-dinaphthylene oxide, m. p. 157° (compare Walder, Abstr., 1883, 208), and *phenylene-β-naphthylene oxide*, $\begin{matrix} C_6H_4 \\ | \\ C_{10}H_6 \end{matrix}\!\!>\!O$, m. p. 200°, dissolving in sulphuric acid to a red solution, which on warming becomes first colourless and then deep violet, changing to green on the addition of water. *p*-Cresol and α-naphthol yield *p*-tolyl ether, *di*-p-*tolylene oxide*, m. p. 166°, and *α-naphthylene*-p-*tolylene oxide*, m. p. 155°. *p*-Cresol and β-naphthol yield *p*-tolyl ether, ββ-dinaphthylene oxide, *ββ-dinaphthyl ether*, m. p. 105°, and *β-naphthylene*-p-*tolylene oxide*, m. p. 220°, which with sulphuric acid behaves similarly to phenylene β-naphthylene oxide.

W. G.

Preparation of Acetonechloroform Acetylsalicylate [o-Acetoxybenzoate]. RICHARD WOLFFENSTEIN (D.R.-P. 246383).—The preparation of acetonechloroform *o*-acetoxybenzoate has been previously described (this vol., i, 556); it is now found that the chlorides of other acylated *o*-hydroxybenzoic acids can be employed, and that the tertiary base (quinoline) can be replaced by calcium carbonate in this reaction. F. M. G. M.

[Preparation of Derivatives of 3-m-Aminophenylacetyl-5-formyldiaminobenzoic Acid.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 246668).—When 3-*m*-aminophenylacetylamino-5-formylaminobenzoic acid (annexed formula) is diazotised, coupled with



acetyl-*m*-phenylenediamine, and the *aminoazo*-compound thus obtained combined with carbonyl chloride, it furnishes a symmetrical derivative of carbamide; from this compound the formyl group is eliminated and a *base* obtained, which on subsequent diazotisation and combination with phenylmethylpyrazolone (and other allied compounds) furnishes colouring matters.

A similar reaction with *m*-nitrobenzoyl-2 : 6-tolylenediamine-4-sulphonic acid and other nitro- and sulphonic derivatives is discussed in the original. F. M. G. M.

Action of Heat on p-Sulphamido-o-toluic Acid. JOHN W. NOWELL (*Amer. Chem. J.*, 1912, **48**, 223—241).—It is found that *p*-sulphamido-*o*-toluic acid, unlike *p*-sulphamidobenzoic acid, does not form any amidine compound on heating (compare Rouiller, this vol., i, 584; Nakaseko, i, 452); this is attributed to the effect of the methyl group in the ortho-position to the carboxyl.

p-Sulphamido-*o*-toluic acid, $NH_2{\cdot}SO_2{\cdot}C_6H_3Me{\cdot}CO_2H$, was obtained from *o*-toluidine-*p*-sulphonic acid by the stages sulphotoluonitrile $\longrightarrow$ cyanotolylsulphonyl chloride, $SO_2Cl{\cdot}C_6H_3Me{\cdot}CN$ (m. p. 52·5—53°) $\longrightarrow$ sulphamidotoluonitrile (m. p. 159—160°) $\longrightarrow$ sulphamidotoluic acid. The potassium, *ammonium* (m. p. 169—172°), *ammonium hydrogen* (m. p. 288—289°), and *barium hydrogen* salts were prepared. No trace of amidine compound was found after fusion of the free acid.

On treating the alcoholic solution of the potassium salt of *p*-sulpho-*o*-toluonitrile with hydrogen chloride, a solution of p-*sulpho*-o-*toluamide*, $SO_3H{\cdot}C_6H_3Me{\cdot}CO{\cdot}NH_2$, prismatic crystals, m. p. 276—278°, was obtained, and the *barium* salt was prepared.

The Sandmeyer reaction applied to 2 : 6-dibromosulphanilic acid in the hope of obtaining 2 : 6-dibromosulphobenzonitrile produced an acidic *substance*, yellow needles; *barium* salt, plates.

By treating potassium hydrogen *o*-nitro-*p*-sulphobenzoate successively with phosphorus pentachloride and ammonium hydroxide, p-*sulphamido*-o-*nitrobenzamide*, needles, m. p. 226°, was obtained. This substance offers great resistance to hydrolysis. D. F. T.

Reaction between Organo-magnesium Compounds and Cinnamylidene Esters. IV. Reactions with Methyl α-Methylcinnamylideneacetate. MARIE REIMER and GRACE POTTER REYNOLDS (*Amer. Chem. J.*, 1912, 48, 206—223. Compare Reynolds, Abstr., 1911, i, 860; Reimer and Reynolds, Abstr., 1908, i, 988).—α-Cinnamylidenepropionic acid, CHPh:CH·CH:CMe·CO$_2$H, prepared by heating at 160° a mixture of cinnamaldehyde and propionyl chloride with excess of sodium propionate (compare Perkin, Trans., 1877, 406), was converted into its methyl ester, m. p. 91°.

The action of magnesium phenyl bromide on this ester produces a mixture of two ketones, which are probably the racemates of stereoisomeric forms of *β-phenyl-γ-benzylidene-α-methylbutyrophenone*,

CHPh:CH·CHPh·CHMe·COPh;

the form of lower m. p. (85°), colourless needles, is converted by the action of potassium hydroxide or hydrochloric acid on its alcoholic solution into the other isomeride, needles, m. p. 112°.

The isomeride of higher m. p. when again treated with magnesium phenyl bromide reacts readily, with formation of *ααγ-triphenyl-δ-benzylidene-β-methyl-*n*-butyl alcohol*,

CHPh:CH·CHPh·CHMe·CPh$_2$·OH,

prisms, m. p. 150°, the structure of which is confirmed by oxidation with potassium permanganate in acetone solution to benzoic acid and *γ-hydroxy-αγγ-triphenyl-β-methylbutyrolactone*,

CPh$_2$·CHMe·CHPh·CO$_2$,

needles, m. p. 187°. The chloroform solution of the ketone also immediately decolorises bromine, producing the *dibromide*,

CHPhBr·CHBr·CHPh·CHMe·COPh,

needles, m. p. 180° (decomp.), together with a small quantity of another substance (probably an isomeride), needles, m. p. 115°. The ketone is also oxidised by potassium permanganate in acetone solution, giving benzoic acid and *β-benzoyl-α-phenylbutyric acid*,

COPh·CHMe·CHPh·CO$_2$H,

needles, m. p. 131°; the *methyl* ester, plates, m. p. 105°, when prepared from the acid, was accompanied by a small quantity of a second *ester*, m. p. 87°.

The readily isomerising form of phenylbenzylidenemethylbutyrophenone of low m. p. resists the action of magnesium phenyl bromide, but reacts with bromine, forming the same additive compound (m. p. 180°) as its isomeride; the formation of the dibromide is probably preceded by the conversion of the ketone into the form of higher m. p. On oxidation it gives a *benzoylphenylbutyric acid* (needles, m. p. 145°). As the *methyl* ester of this acid has m. p. 105°, it is suggested that the ester structurally derived from the isomeric acid above (from the ketone, m. p. 112°) is that (m. p. 87°) obtained in small quantity, and that the ester, m. p. 105°, was formed after previous isomerisation of the acid, m. p. 131°, into that of m. p. 145°.

Magnesium benzyl bromide converts methyl α-methylcinnamylideneacetate into *αζ-diphenyl-β-benzyl-γ-methyl-$\Delta^{\alpha\gamma\epsilon}$-hexatriene*,

CHPh:CH·CH:CMe·C(CH$_2$Ph):CHPh,

needles, m. p. 117°, which potassium permanganate oxidises into benzoic

and phenylacetic acids. The above product from the Grignard reaction is accompanied by a yellow oil, b. p. 265°/20 mm., which is *β-benzyl-γ-benzylidene-α-methylpropyl benzyl ketone*,

$$CHPh:CH\cdot CH(CH_2Ph)\cdot CHMe\cdot CO\cdot CH_2Ph\ ;$$

this is not affected by magnesium ethyl bromide, and although it reacts with bromine no solid product could be separated.

The action of magnesium ethyl bromide on methyl α-methylcinnamylideneacetate gives a mixture of substances from which *δ-benzylidene-β-methyl-αα-diethyl-δ-crotonyl alcohol*,

$$CHPh:CH\cdot CH:CMe\cdot CEt_2\cdot OH,$$

a mobile, yellow liquid, b. p. 200°/20 mm., could be isolated after boiling with alcoholic potassium hydroxide. An *ester*, m. p. 185°, and an *acid*, m. p. 207°, also obtained after this treatment were probably not primary products of the Grignard reaction. D. F. T.

[Preparation of 4 : 6-Dichloro-*m*-tolylthiolacetic Acid and of 4-Chloro-3 : 6-dimethyl-1-phenylthiolacetic Acid.] KALLE & Co. (D.R.-P. 246265. Compare this vol., i, 557).—The conversion of ψ-cumylthiolacetic acid into a dye by the action of fuming sulphuric acid has previously been described; it is now found that if the methyl groups in this compound are replaced by chlorine, variations in colour are produced.

4 : 6-*Dichloro*-m-*tolylthiolacetic acid* and 4-*chloro*-3 : 6-*dimethylphenylthiolacetic acid* are readily prepared from the corresponding bases by diazotisation, xanthogenation, hydrolysis, and subsequent combination with chloroacetic acid; they form brownish-white powders, which may be crystallised from water. F. M. G. M.

Derivatives of Diphenyl. B. F. FORTINSKY (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 781—787).—The author describes preliminary attempts to prepare an indigotin derivative with a hydrogen atom of the benzene nucleus replaced by phenyl, the method employed by Blank (Abstr., 1898, i, 589) being applied to the aminodiphenyls as starting products.

o- and *p*-Aminodiphenyls have the same m. p., 49°, the benzoyl derivatives melting respectively at 88° and 229—229·5°.

Ethyl p-*phenylanilinomalonate*, $C_6H_4Ph\cdot NH\cdot CH(CO_2Et)_2$, prepared by the interaction of *p*-aminodiphenyl (2 mols.) and ethyl bromomalonate (1 mol.), forms colourless, acicular crystals, m. p. 59·5—60°. Attempts to prepare the corresponding indoxylic ester,

$$C_6H_3Ph{<}{}^{CO}_{NH}{>}CH\cdot CO_2Et,$$

by heating this compound at 200—210° did not give a pure product. T. H. P.

Benzylpyruvic Acid. J. BOUGAULT (*Compt. rend.*, 1912, **155**, 477—480).—Fittig's method for the preparation of this acid (Abstr., 1898, i, 196) has been improved by treating α-hydroxy-γ-phenylcrotonamide, instead of the corresponding acid, with alkalis. The products of condensation of the acid with itself and with acetone are described.

In the alkaline hydrolysis of the amide, benzylpyruvic acid is the chief product, but two other substances are formed. The first of these is a *monobasic acid*, $C_{20}H_{17}O_3N$, m. p. 298°, very soluble in chloroform, sparingly soluble in ether, and giving alkali salts soluble in hot water. The second is a *dibasic acid*, $(C_{10}H_{10}O_3)_2,1{\cdot}5H_2O$, which melts at 100—105°, is dehydrated to a transparent mass, and then re-melts at 165° (approx. decomp.). It is readily soluble in ether or alcohol, but insoluble in chloroform.

Benzylpyruvic acid in presence of cold sodium hydroxide solution undergoes aldol-condensation, forming the *dibasic acid*,

$$CH_2Ph\cdot CH_2\cdot C(CH_2Ph\cdot CH\cdot CO\cdot CO_2H)(OH)\cdot CO_2H,$$

m. p. 168—169° (decomp.), soluble in ether, but not in chloroform, and which is hydrolysed by boiling dilute sodium hydroxide solution to benzylpyruvic acid, and with boiling dilute acid forms the *lactone*,

$$\left.\begin{array}{l} CH_2Ph\cdot CH_2\cdot C\text{——}O \\ \qquad CH_2Ph\cdot CH\cdot CO \end{array}\right> CO,$$

m. p. 118°, very soluble in alcohol or ether, but insoluble in light petroleum.

Benzylpyruvic acid condenses with acetone to form two products. The *first*, $CH_2Ph\cdot CH_2\cdot C(CH_2\cdot COMe)(OH)\cdot CO_2H,H_2O$, m. p. 61° or 98° (anhydrous), is hydrolysed by hot dilute alkalis to several products, including benzylpyruvic acid, and is dehydrated by hydrochloric acid, forming a new *acid*, $C_{13}H_{14}O_3$, m. p. 95°. The *second product*,

$$CO_2H\cdot C(OH)(CH_2\cdot CH_2Ph)\cdot CH_2\cdot CO\cdot CH_2\cdot C(OH)(CH_2\cdot CH_2Ph)\cdot CO_2H,$$

m. p. 178°, is soluble in alcohol, but insoluble in chloroform, and yields with hydrochloric acid two dehydration products, the one, $C_{23}H_{20}O_4$, m. p. 124°, being neutral and probably an anhydride or a dilactone, and the other a dibasic acid, m. p. 146°, sparingly soluble in ether.

T. A. H.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXVII. Acid Esters of Nitrohemipinic Acid. RUDOLF WEGSCHEIDER and NOE L. MÜLLER (*Monatsh.*, 1912, **34**, 899—910. Compare this vol., i, 464).—It is now found that of the three supposed isomeric acid esters of nitrohemipinic acid, that of m. p. 115—117° is in reality an eutectic mixture of the other two (compare Wegscheider and von Rušnov, Abstr., 1908, i, 793). This is proved by the possibility of extracting the 2-methyl ester compound (m. p. 140—142°) from the compound of lower m. p. with water, and also by the fact that a mixture of this ester with the 1-methyl ester compound (m. p. 147—149°) in the proportion 2 : 3 forms an eutectic mixture, m. p. 115—116°.

Nitrohemipinic acid, 1-methyl hydrogen nitrohemipinate, and 2-methyl hydrogen nitrohemipinate have electrical conductivities, K 1·986 (for dissociation of the first hydrogen atom), 1·28, and 1·47 respectively. Calculation from the last two numbers as to the conductivity of such a mixture as that suspected in the compound of low m. p. gives a result in good agreement with the experimental.

In one experiment indications of a labile form (m. p. 128°) of the 2-methyl ester were observed.

D. F. T.

Induced Molecular Asymmetry in Unsaturated Compounds. EMIL ERLENMAYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1912, 43, 445—452).—By the reduction of optically active phenylbromolactic acid with zinc in the presence of alcohol, one molecule of active phenyl-lactic acid and one of inactive cinnamic acid are formed according to the equation: $2CHPh(OH)\cdot CHBr\cdot CO_2H + 2H_2 = CHPh\!:\!CH\cdot CO_2H + CHPh(OH)\cdot CH_2\cdot CO_2H$. In spite of the fact that an inactive cinnamic acid is isolated, the alcoholic solution in which the reaction is carried out shows no diminution (in fact, a slight increase) in optical activity after the reduction. As explanation of this fact, it is assumed that the active phenyl-lactic acid can induce an optical activity in the cinnamic acid, which becomes, however, racemised during the subsequent process of isolation. In support of this explanation, it is shown that when equimolecular proportions of inactive storax cinnamic acid and active phenyl-lactic acid are warmed in alcoholic solution with zinc oxide or zinc bromide, the optical activity is doubled. If bromine is added to such an alcoholic mixture of the zinc salts, the cinnamic acid is converted into the dibromide, and it was found that if bromine is added to the mixture of the zinc salts of *d*-phenyl-lactic acid and cinnamic acid, obtained in the way described, a *l*-dibromocinnamic acid can be isolated. If the *l*-lactic acid is employed instead of the *d*-acid, a *d*-dibromocinnamic acid is obtained. The authors contend that the formation of bromo-derivatives of opposite optical activity to the lactic acids employed is consistent with their former results. S. B. S.

Preparation of Amides, Carbamides, or Esters of Cinnamic Acids containing Iodine in the Side-chain, Their Homologues, and Substitution Products. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 246165).—When di-iodocinnamic acid (Abstr., 1891, 1483) is treated with phosphorus pentachloride in chloroform solution, it yields a crystalline *chloride*; this furnishes the corresponding *amide*, which crystallises from acetic acid and decomposes violently when heated to about 200°.

The *carbamide*, m. p. 185—186°, is prepared by heating the foregoing chloride with carbamide ($2\frac{1}{2}$ mols.) at 100°; if the carbamide is replaced by glycine ethyl ester, it furnishes a *compound*, needles, m. p. 149—150°.

When an acetic acid solution of ethyl phenylpropiolate (Trans., 1884, 45, 174) is treated with iodine (2 parts) at 70—80°, and stirred during twelve to fourteen hours, it yields a crystalline *ester*, m. p. 63°.

Guaiacyl β-iodocinnamate, yellow, prismatic crystals, m. p. 131°, is prepared by heating *β-iodocinnamyl chloride* (prepared from the corresponding acid, Abstr., 1902, i, 32) with guaiacol in carbon tetrachloride.

Phenylpropiolamide (Abstr., 1893, i, 163) when treated with iodine furnishes the corresponding *iodoamide* in the form of needles, whilst *ethyl* p-*nitrodi-iodocinnamate*, yellow, prismatic crystals, m. p. 89°, is prepared by shaking ethyl *p*-nitrophenylpropiolate (Abstr., 1882, 846) with an acetic acid solution of iodine during thirty hours at 80°.

F. M. G. M.

Constitution of Certain Trimethoxyphthalic Acids. GUIDO BARGELLINI and OLIMPIA MOLINA (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 146—150).—By the method described below the authors have prepared an acid which must undoubtedly be 3 : 4 : 5-trimethoxy-*o*-phthalic acid; this is identical in properties with the acid obtained by Windaus (Abstr., 1911, i, 904) by oxidising colchicine, and regarded by him as 3 : 4 : 6-trimethoxy-*o*-phthalic acid, owing to its non-identity with the supposed 3 : 4 : 5-trimethoxy-*o*-phthalic acid described by Feist (Abstr., 1908, i, 100); the last-named acid was obtained by etherifying Sennhofer and Brunner's pyrogalloldicarboxylic acid (Abstr., 1881, 267) by means of diazomethane. The conclusion must therefore be drawn that Windaus's acid is 3 : 4 : 5-trimethoxy-*o*-phthalic acid, and that the colchicine molecule contains three methoxy-groups arranged vicinally, and not in the 1 : 2 : 4-positions, as Windaus assumed.

It is evident, also, that Feist's acid cannot have the constitution attributed to it by this author, and Voswinckel and de Weerth (this vol., i, 472), on other grounds, regard it as 4 : 5 : 6-trimethoxy*iso*-phthalic acid.

3 : 4 : 5-*Trimethoxytrichloromethylphthalide*,

$$C_6H(OMe)_3<\begin{matrix}CO\\CH(CCl_3)\end{matrix}>O,$$

obtained by the action of chloral on methyl trimethylgallate (methyl 3 : 4 : 5-trimethoxybenzoate) in presence of concentrated sulphuric acid (compare Fritsch, Abstr., 1898, i, 663), has m. p. 70—71°, and gives the normal molecular weight in freezing benzene. Treatment of this compound with alkali converts it into 3 : 4 : 5-*trimethoxycarboxyphthalide*, $C_6H(OMe)_3<\begin{matrix}CO\\CH(CO_2H)\end{matrix}>O$, m. p. 142—143°, which loses CO_2 when heated, giving 3 : 4 : 5-*trimethoxyphthalide*, $C_6H(OMe)_3<\begin{matrix}CO\\CH_2\end{matrix}>O$, m. p. 134—135°. Oxidation of this by means of permanganate gives 3 : 4 : 5-trimethoxy-*o*-phthalic acid, m. p. 174°; the *anhydride* of this acid, m. p. 143°; the *imide*, $C_6H(OMe)_3<\begin{matrix}CO\\CO\end{matrix}>NH$, m. p. 180°, giving a fluorescent alcoholic solution, and the anilide were prepared.

3 : 4 : 5-*Trimethoxyphthalanilic acid*,
$C_6H(OMe)_3(CO\cdot NHPh)\cdot CO_2H[(OMe)_3:CO\cdot NHPh:CO_2H = 3:4:5:2:1]$, has m. p. 187—188°.

All these compounds, including methyl trimethylgallate, dissolve in concentrated sulphuric acid, giving colourless or pale yellow solutions. Addition of increasing quantities of nitric acid to these solutions gives successively intense violet, wine-red, and pale yellow colorations. A sulphuric acid solution of colchicine gives a similar succession of colours with nitric acid. T. H. P.

The Phthalyl Cyanides. GIBBS BLACKSTOCK (*J. Amer. Chem. Soc.*, 1912, 34, 1080—1082).—*Phthalyl*, iso*phthalyl*, and *terephthalyl cyanides* can be prepared by (*a*) the action of hydrocyanic acid on a solution of the acid chloride in anhydrous ether containing some pyridine, when a white *substance* first precipitates (possibly a com-

pound of acetyl chloride and pyridine), the crude cyanide separating subsequently as a dark oil; (*b*) digesting the acid chloride in acetone solution with mercuric cyanide; (*c*) heating the acid chloride with mercuric cyanide in a sealed tube at 140—160°. Method (*b*) is not very satisfactory, and phthalyl cyanide prepared by method (*a*) is difficult to purify.

The three cyanides are brown powders, which become viscous near 300° with apparent decomposition; they are not hydrolysed when heated with hydrochloric acid in a sealed tube, but when heated with potassium hydroxide solution a little ammonia is formed. D. F. T.

The Acylation of Amino-acids and Some Ketolactimones. J. D. Riedel (*Chem. Zentr.*, 1912, i, 1773—1774; from *Riedel's Ber.*, 1912, 13—24).—Experiments on the acylation of arylaminoacetates with succinic and camphoric anhydrides show that anthranilic acid is better suited in some cases to the characterisation of dicarboxylic anhydrides than aniline. Phthalic and citraconic anhydrides are less suitable for acylation.

Chloroacetylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2Cl$, has m. p. 184°. *Hydroxyacetylanthranilolactone*, $C_6H_4<\begin{matrix}NH\cdot CO\\CO—O\end{matrix}>CH_2$, from chloroanthranilic acid and boiling aqueous sodium carbonate, forms red leaflets, m. p. 200°. Solution in sodium hydroxide and precipitation gives *hydroxyacetylanthranilic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot OH,$$

m. p. 181°. iso*Valerylanthranilic acid* forms colourless prisms, sintering at 105°, m. p. 114—115°; *a-bromo*iso*valerylanthranilic acid* is white, m. p. 147—148°, and passes into *a-hydroxy*iso*valerylanthranilolactone*, $C_6H_4<\begin{matrix}NH\cdot CO\\CO—O\end{matrix}>CH\cdot CHMe_2$, m. p. 181°, from which the *hydroxy-acid*, m. p. 175°, is obtained.

Succinanilcarboxylic acid, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, has m. p. 186°, and behaves as a strong dibasic acid. *Anthranoylcamphoric acid*, $C_{17}H_{21}O_5N$, forms small needles, m. p. 198—199°.

When benzylchloroamide, $C_6H_5\cdot CO\cdot NHCl$, is used, sufficient alkali must be present to convert it into a salt, $C_6H_5\cdot C(ONa)NCl$, as well as the amino-acid, and the product is then, in the case of anthranilic acid, not *o*-benzoylhydrazinobenzoic acid, but the isomeric o-*phenylcarbamidobenzoic acid*, $CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot NHPh$, m. p. 190—192°, from which *phenyldiketotetrahydroquinazoline*, $C_{14}H_{10}O_2N_2$, m. p. 278—280°, is obtained by heating, or by evaporation with ammonia. A by-product of the acylation is *phenylbenzoylcarbamide*,

$$NHPh\cdot CO\cdot NH\cdot COPh,$$

m. p 206—208°. C. H. D.

p-Iodobenzaldehyde and Derivatives with Uni- and Multi-valent Iodine. Conrad Willgerodt and Alexis Ucke (*J. pr. Chem.*, 1912, [ii], 86, 276—283).—On treatment with chlorine in chloroform solution, *p*-iodobenzaldehyde yields a stable *iododichloride*,

$$ICl_2\cdot C_6H_4\cdot CHO,$$

which is converted by aqueous sodium carbonate into p-*iodosobenzalde-*

hyde, $IO\cdot C_6H_4\cdot CHO$. The latter compound reacts with *p*-iodoxytoluene and silver oxide in the presence of water, yielding an alkaline, aqueous solution of p-*aldehydophenyl*-p-*tolyliodonium hydroxide*,

$$C_6H_4Me\cdot I(OH)\cdot C_6H_4\cdot CHO,$$

which could not be isolated and, therefore, was characterised by the preparation of the following salts: the *chloride*, prepared by saturating the aqueous solution of the base with sodium chloride, crystallises in small, colourless plates, m. p. 132°; the amorphous, orange-yellow *platinichloride*, $(C_6H_4Me\cdot ICl\cdot C_6H_4\cdot CHO)_2PtCl_4$, decomposes at 173°; the *bromide* crystallises in small, transparent needles, m. p. 154—155°. The *iodide* forms aggregates of pale yellow, microscopic pyramids, has m. p. 150—151° when slowly heated, and is converted by iodine in alcoholic solution into a *tri-iodide*, $C_{14}H_{12}OI_4$, which forms long, brown to black needles, m. p. 95°; the *acetate*, long, colourless needles, m. p. 265°, and unstable *dichromate* are also described.

p-Aldehydophenyl-*p*-tolyliodonium bromide forms a light yellow, amorphous *phenylhydrazone*, $C_6H_4Me\cdot IBr\cdot C_6H_4\cdot CH:N\cdot NHPh$, m. p. 134°, and a *semicarbazone*, $C_{15}H_{15}ON_3BrI$, crystallising in short, colourless needles, m. p. 216°. It reacts with aqueous hydrazine sulphate, yielding a pale yellow *azine*, $N_2(CH\cdot C_6H_4\cdot IBr\cdot C_6H_4Me)_2$, m. p. 185°, and with benzidine in hot alcoholic solution to form the *compound*,

$$NH_2\cdot C_6H_4\cdot C_6H_4\cdot N:CH\cdot C_6H_4\cdot IBr\cdot C_6H_4Me,$$

an amorphous, yellow powder, m. p. 155°. On account of its instability the oxime could not be isolated.

Di-p-*iodobenzoin*, $C_6H_4I\cdot CH(OH)\cdot CO\cdot C_6H_4I$, prepared by condensing *p*-iodobenzaldehyde with potassium cyanide in methyl-alcoholic solution, crystallises in colourless needles, m. p. 122°, and on treatment with chlorine in chloroform solution yields on unstable *iododichloride*; the *benzoyl* derivative forms long, colourless, strongly refractive needles, m. p. 152°, and also yields an unstable *iododichloride*.

Di-p-*iodobenzil*, $C_6H_4I\cdot CO\cdot CO\cdot C_6H_4I$, prepared by oxidising di-*p*-iodobenzoin with nitric acid, crystallises in yellow needles, m. p. 255°.

F. B.

Bromination of *m*-Hydroxybenzaldehyde, Vanillin, and Homovanillic Acid. ROLAND PSCHORR (*Annalen*, 1912, 391, 23—39).—The following compounds of definite constitution have been prepared for the synthesis of phenanthrene derivatives.

[With W. SELLE, W. KOCH, H. STOOF, and O. TREIDEL.]—6-*Bromo-3-hydroxybenzaldehyde*, m. p. 135° (corr.), slender, colourless needles, obtained by the bromination of a 10% chloroform solution of *m*-hydroxybenzaldehyde, yields a *semicarbazone*, m. p. 253° (corr.), and is converted by methyl sulphate and alkali into 6-*bromo-3-methoxybenzaldehyde*, m. p. 75—76° (*semicarbazone*, m. p. 251° [corr.]). This substance, which is also produced by the bromination of *m*-methoxybenzaldehyde in boiling chloroform, is oxidised in acetone by aqueous potassium permanganate to 6-*bromo-3-methoxybenzoic acid*, m. p. 161—162° (corr.), the orientation of the substituents in which is known by the formation of the same acid from 6-nitro-3-methoxybenzoic acid. 6-*Amino-3-methoxybenzoic acid* yields yellow needles, m. p. 149°, by crystallisation, and colourless needles, m. p. 150°, by

sublimation. 2-*Amino-3-methoxybenzoic acid*, m. p. 169—170° (corr.), is converted into 2-*bromo-3-methoxybenzoic acid*, m. p. 153—155°, by the usual processes.

A 10% solution of protocatechualdehyde in glacial acetic acid yields by bromination 5-*bromo*-3 : 4-*dihydroxybenzaldehyde*, m. p. 230° (corr.), which forms a *phenylhydrazone*, m. p. 138—140°, *diacetyl* derivative, m. p. 82—84° (corr.), and *dimethyl ether*, m. p. 62—64° (*semicarbazone*, m. p. 202—203° [corr.]). 5-Bromovanillin, obtained by the bromination of vanillin in chloroform at 0°, is converted into the preceding dimethyl ether by methyl sulphate and alkali. The position of the halogen atom in these compounds is ascertained by the conversion of the dimethyl ether into 5-bromo-3 : 4-dimethoxybenzoic acid by 20% potassium permanganate or by methyl-alcoholic potassium hydroxide; by the latter method, 5-bromoprotocatechuic acid and 5-*bromoveratryl alcohol*, b. p. 190°/12 mm., are also produced. The bromination of vanillin methyl ether in glacial acetic acid at the ordinary temperature yields 6-*bromo*-3 : 4-*dimethoxybenzaldehyde*, m. p. 149—150° (corr.), the *oxime* of which, m. p. 167—168° (corr.), is converted by boiling acetic anhydride into 6-bromo-3 : 4-dimethoxybenzonitrile, m. p. 118—119° (corr.). The nitrile yields Zincke's 6-bromo-3 : 4-dimethoxybenzoic acid by treatment with boiling *N*/10-sodium hydroxide. This acid, together with 6-*bromo*-3 : 4-*dimethoxybenzyl alcohol*, m. p. 88—91°, is also obtained from 6-bromo-3 : 4-dimethoxybenzaldehyde and methyl-alcoholic potassium hydroxide.

By bromination in chloroform, *ethyl* 4-*hydroxy*-3-*methoxyphenylacetate* (*ethyl* α-*homovanillate*), b. p. 180—185°/13—15 mm., yields *ethyl* 6-*bromo*-4-*hydroxy*-3-*methoxyphenylacetate*, m. p. 95°, by the hydrolysis of which 6-*bromo*-4-*hydroxy*-3-*methoxyphenylacetic acid*, m. p. 180—181°, is obtained; its *acetyl* derivative, m. p. 170—171° (corr.), is prepared by the bromination of acetyl-α-homovanillic acid. By treating its alkaline solution with methyl sulphate, the preceding brominated ester is converted into *ethyl* 6-*bromo*-3 : 4-*dimethoxyphenylacetate*, by the hydrolysis of which 6-*bromo*-3 : 4-*dimethoxyphenylacetic acid*, m. p. 115—116° (corr.), is obtained; the same acid is produced, in smaller yield, by the bromination of 3 : 4-dimethoxyphenylacetic acid.

The position of the halogen atom in the preceding compounds is deduced as follows. It is not in position-5, because 5-*bromo*-3 : 4-*dimethoxyphenylacetic acid*, prepared from 5-*bromoveratryl chloride*, m. p. 56—59°, through the nitrile, has m. p. 95—98° (corr.). The following experiments show that the bromine is not in position-2. By condensation with *o*-nitrobenzaldehyde, the bromo-3 : 4-dimethoxyphenylacetic acid will yield a 3 : 4- or a 2 : 3-dimethoxyphenanthrene derivative according as the bromine is in position 6 or 2. The former is obtained; thus *o*-nitrobenzaldehyde and sodium 6-bromo-3 : 4-dimethoxyphenylacetate, by heating with acetic anhydride at 100° for sixty hours, yield *o*-*nitro*-α-6-*bromo*-3 : 4-*dimethoxyphenylcinnamic acid*, $NO_2\cdot C_6H_4\cdot CH:C(CO_2H)\cdot C_6H_2Br(OMe)_2$, m. p. 199—200° (corr.), yellow crystals. The reduction of the latter by ferrous sulphate and aqueous ammonia at about 93° yields the *amino*-compound, m. p. 194—195° (corr.), which is converted in the usual manner into

1-*bromo*-3 : 4-*dimethoxyphenanthrene*-10-*carboxylic acid*, decomp. 220°, sintering at 168—175°. By eliminating the bromine by boiling alcohol, $N/1$-sodium hydroxide, and copper-zinc dust, the latter is converted into 3 : 4-*dimethoxyphenanthrene*-10-*carboxylic acid*, m. p. 185—186°.

[With O. TREIDEL.]—By reactions similar to the preceding, o-*nitro*-α-2 : 3-*dimethoxyphenylcinnamic acid*, m. p. 190° (corr.), yellow needles, prepared from *o*-nitrobenzaldehyde and sodium α-homoveratrate, is converted through the *amino-acid*, m. p. 173° (corr.), yellow plates, into 2 : 3-*dimethoxyphenanthrene*-10-*carboxylic acid*, m. p. 254° (corr.); the latter yields 2 : 3-dimethoxyphenanthrene by distillation under 100—150 mm. C. S.

Preparation of Aldehydes of the Aromatic Series with at least one Hydroxy-group next to the Aldehyde Group. KALLE & Co. (D.R.-P. 246338).—When "thioindigo scarlet" (prepared by the condensation of isatin with oxythionaphthen) is heated with a 40% solution of sodium hydroxide, it yields *o*-thiolbenzoic acid and *oxindolaldehyde*, $C_6H_4<\begin{smallmatrix}C(CHO)\\NH\end{smallmatrix}>C{\cdot}OH$, yellow needles, m. p. 213°, which condenses with anthranilic acid to furnish an *azomethine*.

Acenaphthenonaldehyde, colourless leaflets, is prepared in a similar manner from the condensation product of 3-oxy-(1)-thionaphthen and acenaphthenquinone. F. M. G. M.

Action of Zinc on a Mixture of *cyclo*Hexanone and Allyl Iodide. MICHAEL SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1013—1025).—1-Allyl*cyclo*hexanol, $OH{\cdot}C_6H_{10}{\cdot}C_3H_5$, obtained by the action of zinc on a mixture of *cyclo*hexanone and allyl iodide, is a colourless, mobile liquid, b. p. 188—192° (compare Matschurevitsch, Abstr., 1911, i, 961). On oxidation it yields: (1) the *trihydric alcohol*,

$$CH_2<\begin{smallmatrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{smallmatrix}>C(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

which forms spherical aggregates of acicular crystals, and (2) 1-cyclo*hexanol*-1-*acetic acid*, $OH{\cdot}C_6H_{10}{\cdot}CH_2{\cdot}CO_2H$, the *calcium*, *lead*, and *zinc* salts of which were analysed.

1-*Chloro*-1-*allyl*cyclo*hexane*, $C_6H_{10}Cl{\cdot}CH_2{\cdot}CH{:}CH_2$, is a colourless liquid, b. p. 89—92°/21 mm., D_0^0 1·00275, D_{20}^{20} 0·98744, D_4^{20} 0·98616. When treated with silver carbonate, it is converted into the *hydrocarbon*, C_9H_{14}, which is a liquid, b. p. 159—161°, D_0^0 0·8611, D_{20}^{20} 0·8468, D_4^{20} 0·8457, and combines with bromine, giving the compound, $C_9H_{14}Br$, as a yellow, viscous liquid. The positions of the double linkings in the hydrocarbon are being investigated.

T. H. P.

Action of Sodamide on αδ-Dibenzoylbutane. EDOUARD BAUER (*Compt. rend.*, 1912, **155**, 288—291).—Haller and Bauer (Abstr., 1909, i, 108, 654) have studied the action of sodamide on phenyl acyl ketones having at least one atom of hydrogen attached to the carbon atom in the α-position to the ketonic group. This study has now been extended to the diketones.

$\alpha\delta$-Dibenzoylbutane (1 mol.) when warmed in benzene solution with sodamide (2 mols.) turns red, and a precipitate is formed. At the end of the reaction (30—45 minutes) the product is decomposed with ice water, and the oil distilled under reduced pressure, a viscid liquid passing over at 218—220°/13 mm. On cooling, this solidifies and can be separated by crystallisation into two substances, one crystallising in slender needles, m. p. 98°, the other in stout, yellow prisms, m. p. 53°. Analysis shows them to be isomerides of the formula $C_{18}H_{16}O$, formed by the dehydration of the dibenzoylbutane. On oxidation by potassium permanganate, the isomeride, m. p. 53°, yields γ-benzoylbutyric acid and benzoic acid, whilst the isomeride, m. p. 98°, yields succinic and benzoic acids, thus showing them to be stereoisomerides, 1-*benzoyl*-2-*phenyl*-Δ^1-cyclo*pentene*, $CH_2<\begin{matrix}CBz\colon CPh\\ CH_2\cdot CH_2\end{matrix}$, m. p. 53°, and 1-*benzoyl*-2-*phenyl*-Δ^2-cyclo*pentene*, $CH_2<\begin{matrix}CHBz\cdot CPh\\ CH_2-CH\end{matrix}$, m. p. 98°, formed by the elimination of water from the intermediate unstable 1-benzoyl-2-phenyl*cyclo*pentan-2-ol.

By prolonging the action of the sodamide for three or four hours the results are very different, benzamide, a substance, $C_{12}H_{13}ON$, m. p. 135°, and an unsaturated hydrocarbon, $C_{11}H_{12}$, b. p. 110°/13 mm., being obtained in addition to the above *cyclo*pentenes. W. G.

Cyclic Hexamethylenic β-Diketones. GEORGES LESER (*Ann. Chim. Phys.*, 1912, [viii], **26**, 227—257).—A connected account of work published already (Abstr., 1899, i, 479, 743; 1900, i, 430; 1901, i, 271; 1902, i, 261, 550; 1910, i, 48. The following new data are recorded.

2-*Acetyl*cyclo*hexanone*, D^0 1·075, n_D 1·5138, b. p. 111—112°/18 mm., prepared by condensing *cyclo*hexanone with ethyl acetate in presence of sodium, has a cumin-like odour, yields a *copper* derivative (steel-grey spangles), a *dioxime* (m. p. 149°), and a *semicarbazone* (m. p. 162—163). The diketone dissolves in alkalis, but, on standing, the solution deposits *cyclo*hexanone; in warm alkalis the hydrolysis proceeds further, ω-acetylhexoic acid being formed (Kipping and Perkin, Trans., 1889, **55**, 338). The potassium derivative of the diketone reacts in the cold with ethyl iodide in alcohol, forming the 2-*ethyl* derivative, b. p. 238—240°, which is liquid, yields a viscous *oxime*, and on hydrolysis with hot dilute alkalis yields 2-*ethyl*cyclo*hexanone*, b. p. 182—183°.

4-Acetyl-1-methyl*cyclo*hexan-3-one (Abstr., 1900, i, 430), n_D 1·5012, b. p. 230—231°/740 mm., on treatment with ammonia solution gives a crystalline *compound*, $C_9H_{15}ON$, m. p. 102°, which is not decomposed by boiling dilute sodium hydroxide solution. 4-Acetyl-1 : 4-dimethyl-*cyclo*hexan-3-one (Abstr., 1901, i, 278) has n_D 1·4669, D^{13} 1·007, b. p. 246—247°, and its homologue, 4-*acetyl*-1-*methyl*-4-*ethyl*cyclo*hexan*-3-*one*, has b. p. 255—260°; neither reacts with the Grignard reagent.

ϵ-Acetyl-$\delta\delta$-dimethyl-n-hexoic acid (Abstr., 1899, i, 743) yields an *ethyl* ester, b. p. 148—150°, and on reduction by sodium in alcohol

gives the corresponding *hydroxy-acid*, m. p. 61°, crystallising in silky tufts.

The product formed by the dehydration of 2-acetyl-1 : 1 : 3-trimethyl*cyclo*hexan-3-ol (Abstr., 1910, i, 48) is now shown to be 2-acetyl-1 : 1 : 3-trimethyl-Δ^2-*cyclo*hexene, since it yields $\alpha\alpha$-dimethyladipic acid on oxidation by permanganate. The same product on reduction with sodium furnishes the corresponding unsaturated *alcohol*, D^{13} 0·933, n_D 1·4864, b. p. 217°, a liquid having an odour recalling that of ozone and yielding an *acetyl* derivative, b. p. 231—232°.

4-Acetyl-1 : 1-dimethyl*cyclo*hexan-3-one (Abstr., 1902, i, 261 ; 1910, i, 48) on hydrolysis by alkalis yields chiefly the corresponding cyclanone, but also some *ε-acetyl-ββ-dimethyl-*n*-hexoic acid*,

$$CH_2Ac\cdot[CH_2]_2\cdot CMe_2\cdot CH_2\cdot CO_2H$$

(crystalline *oxime*, m. p. 93°), whilst its potassium derivative reacts with methyl iodide to form 4-*acetyl*-1 : 1 : 4-*trimethyl*cyclo*hexan*-3-*one*, b. p. 122—124°/20 mm. or 229—230°/747 mm., m. p. 43°, which does not give the characteristic reactions of the β-diketones, and yields a *monoxime*, m. p. 159°, crystallising in voluminous prisms. In this and similar cases it is probably the carbonyl group in the side-chain which does not react with hydroxylamine. T. A. H.

Semicyclic 1 : 5-Diketones of the *cyclo*Pentane Series. HANS STOBBE (*J. pr. Chem.*, 1912, [ii], 86, 209—218. Compare Abstr., 1902, i, 472 ; 1903, i, 115 ; 1909, i, 309, and the following abstracts).—Under the influence of alkali hydroxides and secondary amines, *cyclo*pentanone combines with ketones of the type $CHR\!:\!CH\cdot COPh$ (where $R = C_6H_5\cdot$, *p*-$MeO\cdot C_6H_4\cdot$, or *mp*-$CH_2\!:\!O_2\!:\!C_6H_3\cdot$), yielding 1 : 5-diketones, $COPh\cdot CH_2\cdot CHR\cdot CH<\begin{array}{l}CH_2\cdot CH_2\\ CO—CH_2\end{array}$, which are decomposed into their components by distillation under ordinary pressure. The diketones readily form disemicarbazones, and react with hydroxylamine, yielding either monoximes or dioximes ; when boiled with hydroxylamine hydrochloride in alcoholic solution they are converted into dihydropyrindene derivatives, $\begin{array}{l}CH\cdot CR\!:\!C\cdot CH_2\\ CPh—N\!:\!C\cdot CH_2\end{array}>CH_2$, which form stable salts and may also be obtained by the action of hydrogen chloride on solutions of the oximes.

The diketones condense with benzaldehyde, anisaldehyde, and piperonaldehyde to form compounds of the type $COPh\cdot CH_2\cdot CHR<\begin{array}{l}CH_2\cdot CH_2\\ CO—C\!:\!CHR'\end{array}$, which often occur in two stereoisomeric forms. The constitution of these condensation products has been established by the behaviour of the isomeric anisylidene compounds (I and II below) ; on distillation these decompose in two ways, (1) into acetophenone and two stereoisomeric benzylideneanisylidene*cyclo*pentanones, $\begin{array}{c}CH_2—CH_2\\ CHPh\!:\!C\cdot CO\cdot C\!:\!CH\cdot C_6H_4\cdot OMe\end{array}$, and (2) into phenyl styryl ketone and anisylidene*cyclo*pentanone, which at a higher temperature further decomposes into *cyclo*pentanone and dianisylidene*cyclo*pentanone. Since both isomerides yield the same products, the con-

clusion is drawn that the anisylidene compounds are stereoisomeric, as represented in the following formulæ :

$$\text{I.}\ \begin{array}{l} \mathrm{CHPh\cdot CH\cdot CH_2}\!>\!\mathrm{CH_2} \\ \mathrm{CH_2 \quad CO\!-\!-\!C} \\ \mathrm{COPh \quad H\cdot C\cdot C_6H_4\cdot OMe} \end{array} \qquad \text{II.}\ \begin{array}{l} \mathrm{CHPh\cdot CH\!-\!-\!-\!CH_2}\!>\!\mathrm{CH_2} \\ \mathrm{CH_2 \quad CO\!-\!-\!-\!-\!C} \\ \mathrm{COPh \quad OMe\cdot C_6H_4\cdot C\cdot H} \end{array}$$

and this view is confirmed by the interconversion of the two forms by exposure to light, or by boiling them with a solution of iodine in benzene. F. B.

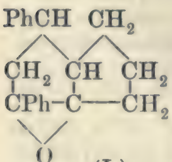
Optically Active Semicyclic 1 : 5-Diketones of the *cyclo*Hexane Series. HANS STOBBE (*J. pr. Chem.*, 1912, [ii], 86, 218—225. Compare following abstracts).—*d*-3-Methyl*cyclo*hexanone combines with ketones of the type, $\mathrm{CHR{:}CH\cdot COPh}$ (where R = $\mathrm{C_6H_5}$, $\mathrm{OMe\cdot C_6H_4}$, *mp*-$\mathrm{CH_2{:}O_2{:}C_6H_3}$), yielding two stereoisomeric 1 : 5-diketones, $\mathrm{COPh\cdot CH_2\cdot CHR\cdot CH}\!<\!\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CO\!-\!CH_2}\end{array}\!>\!\mathrm{CHMe}$, of which the less fusible modification is produced in greater quantity. That the two forms are stereoisomeric has been proved by the conversion of each pair of isomerides into one and the same tetrahydroquinoline derivative, $\begin{array}{l}\mathrm{CH\cdot CR{:}C\cdot CH_2\cdot CH_2}\\ \mathrm{CPh\!-\!N{:}C\cdot CH_2\cdot CHMe}\end{array}$, by boiling with hydroxylamine hydrochloride in alcoholic solution.

The above constitution for the diketone has been confirmed in the case of the condensation products from phenyl styryl ketone and its *mp*-methylenedioxy-derivative by the oxidation of one of the isomerides to β-methyladipic acid. F. B.

Semicyclic 1 : 5-Diketones from *cyclo*Pentanone and Phenyl Styryl Ketone. ROBERT GEORGI [and, in part, with HANS VOLLAND] (*J. pr. Chem.*, 1912, [ii], 86, 232—241. Compare Stobbe and Volland, Abstr., 1903, i, 115).—β-Phenyl-β-2-*cyclo*pentanonylpropiophenone is reduced by sodium amalgam in alcoholic or moist ethereal solution to a white, crystalline *dihydroxydiphenylbicyclooctane*,

$$\mathrm{CH_2}\!<\!\begin{array}{l}\mathrm{CHPh\!-\!-\!CH\!-\!-\!CH_2}\\ \mathrm{CPh(OH)\cdot C(OH)\cdot CH_2}\end{array}\!>\!\mathrm{CH_2}.$$

This has m. p. 142—143°, and gives at first an orange and then a red coloration with sulphuric acid. It discharges the colour from a solution of bromine in chloroform, but the decolorised solution rapidly becomes brown again, owing to the liberation of bromine. It forms a *monobenzoyl* derivative, crystallising in prisms, m. p. 91—92°, and a *mono*-m-*nitrobenzoyl* derivative, m. p. 127—128°; attempts to prepare the corresponding diacyl derivatives proved fruitless. The action of phenylcarbamide leads to the formation of a *monophenylurethane*, $\mathrm{C_{27}H_{27}O_3N}$, m. p. 140—142°, together with a light yellow *substance*, m. p. 120—122°.



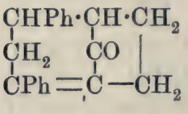
(I.)

When heated with hydriodic acid and phosphorus at 180—190°, the dihydroxy-compound is converted into a yellow oil, the greater part of which dissolves

in a mixture of alcohol and ether, leaving a small amount of a solid *substance*, $C_{20}H_{20}O$, m. p. 126—130°.

If the action is carried out at lower temperatures, solid substances of still lower m. p. may be isolated from the product. Both the oily and solid products have the same composition, and probably represent anhydrides of constitution (I).

β-Phenyl-β-2-*cyclo*pentanonylpropiophenone is reduced by hydriodic acid and phosphorus at 140—150° to a *compound*, $C_{20}H_{22}O_2$, isomeric with the above dihydroxydiphenylbi*cyclo*octane. On treatment with hydrogen chloride in alcoholic solution, the diketone loses water with the formation of a *diphenylbi*cyclo*octenone* (annexed formula). This crystallises in needles, m. p. 122°, and forms a *semicarbazone*, $C_{21}H_{21}ON_3$, m. p. 202—203° (decomp.).



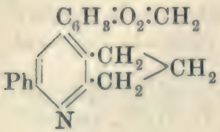
Under the influence of sodium hydroxide in aqueous alcoholic solution, the diketone condenses with benzaldehyde, yielding two stereoisomeric *β-phenyl-β-3-benzylidene*cyclo*pentan-2-onylpropiophenones*, $COPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2\\ CO{-}C{:}CHPh\end{matrix}$, which are separated by fractional crystallisation from alcohol. The more readily soluble isomeride is light yellow in colour, m. p. 104—106°, dissolves in sulphuric acid with a red coloration, and is transformed by exposure to light into the less soluble, colourless isomeride, which has m. p. 143—144°, and gives an orange-yellow coloration with sulphuric acid; the interconversion of the two forms has been effected by boiling with a 0·01% solution of iodine in benzene.

The diketone also condenses with piperonaldehyde, yielding two stereoisomeric *β-phenyl-β-3-piperonylidene*cyclo*pentan-2-onylpropiophenones*, $COPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2\\ CO{-}C{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2\end{matrix}$, of which one is pale yellow, and has m. p. 118—120°, whilst the other isomeride is dark yellow, and has m. p. 143—144°. F. B.

Semicyclic 1 : 5-Diketones Prepared by the Addition of *cyclo*-Pentanone to Phenyl Methylenedioxystyryl Ketone and Phenyl *p*-Methoxystyryl Ketone. CURT STRIEGLER (*J. pr. Chem.*, 1912, [ii], 86, 241—250).—β-m : p-*Methylenedioxyphenyl-β-2-*cyclo*pentanonylpropiophenone*, $\begin{matrix}COPh{\cdot}CH_2\\ CH_2{:}O_2{:}C_6H_3\end{matrix}>CH{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2\\ CO{-}CH_2\end{matrix}$, prepared by the condensation of phenyl *mp*-methylenedioxystyryl ketone with *cyclo*pentanone by means of piperidine or diethylamine, and purified by means of its disemicarbazone, crystallises in clusters of needles, m. p. 120—121°, and is resolved by hot alcoholic potassium hydroxide into its components. It is accompanied by a small quantity of a substance, $C_{37}H_{32}O_7$, crystallising in needles, m. p. 275°.

The *disemicarbazone*, $C_{20}H_{26}O_4N_6$, crystallises with alcohol (1 mol.) in white, felted needles, m. p. 214—215° (decomp.), which lose their alcohol at 100—110° and then have m. p. 215—216°. The *monoxime* crystallises in needles, m. p. 133—134°; the *dioxime*, $C_{21}H_{22}O_4N_2$, in hexagonal leaflets, m. p. 193—194°.

When warmed with hydroxylamine hydrochloride in alcoholic solution the diketone is converted into 5-phenyl-7-*mp*-methylenedioxyphenyl-2 : 3-dihydro-4-pyrindene (annexed formula), which crystallises from alcohol in long, yellow needles, m. p. 124—125°, and forms a yellow, crystalline *hydrochloride*, m. p. 260°, a *hydrogen sulphate*, $C_{21}H_{17}O_2N,H_2SO_4$, m. p. 215°, and a *picrate*, m. p. 189—190° (decomp.).



β-mp-*Methylenedioxyphenyl*-β-3-*piperonylidene*-cyclo*pentan*-2-*onylpropiophenone*,

$$\begin{matrix} CH_2{:}O_2{:}C_6H_3 \\ COPh{\cdot}CH_2 \end{matrix}\!>\!CH{\cdot}CH\!<\!\begin{matrix} CH_2{\cdot}CH_2 \\ CO{-}C{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2 \end{matrix},$$

prepared by condensing the diketone with piperonaldehyde by means of aqueous sodium hydroxide at 0°, crystallises in yellow, pointed prisms, m. p. 178—180°, instantly decolorises bromine, gives with sulphuric acid a yellow coloration which gradually becomes darker, and when heated with 20% alcoholic potassium hydroxide decomposes into acetophenone and dipiperonylidene*cyclo*pentanone (Mentzel, Abstr., 1903, i, 497).

The *anisylidene* derivative, $C_{29}H_{26}O_5$, obtained in a similar manner from the diketone and anisaldehyde, forms white needles, m. p. 140—142°, and resembles the preceding compound in its chemical behaviour; the *benzylidene* derivative, $C_{28}H_{24}O_2$, crystallises in pale yellow prisms, m. p. 128—130°.

β-*Anisyl*-β-2-cyclo*pentanonylpropiophenone*,

$$\begin{matrix} OMe{\cdot}C_6H_4 \\ COPh{\cdot}CH_2 \end{matrix}\!>\!CH{\cdot}CH\!<\!\begin{matrix} CH_2{\cdot}CH_2 \\ CO{-}CH_2 \end{matrix},$$

obtained in an impure condition as an oil by condensing phenyl *p*-methoxystyryl ketone and *cyclo*pentanone with piperidine or diethylamine, forms a *disemicarbazone*, $C_{23}H_{28}O_3N_6$, m. p. 235—236° (decomp.), and is converted by the action of hydroxylamine, or, better, its hydrochloride, into 5-phenyl-7-anisyl-2 : 3-dihydro-4-pyrindene.

$$\begin{matrix} C(C_6H_4{\cdot}OMe){:}C{\cdot}CH_2 \\ CH{:}CPh{-}N{:}C{\cdot}CH_2 \end{matrix}\!>\!CH_2,$$

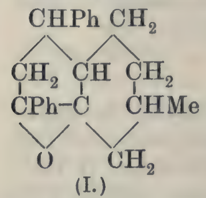
which is pale yellow, has m. p. 144—145°, and forms a *hydrochloride*, m. p. 218°, and a *picrate*, yellow needles, m. p. 185—186°. In one instance the oily product of the condensation deposited a substance, $C_{32}H_{28}O_4$, crystallising in white needles, m. p. 191—192°. F. B.

Stereoisomeric Semicyclic 1 : 5-Diketones from 3-Methyl*cyclo*hexanone and Phenyl Styryl Ketone. ARTHUR ROSENBURG (*J. pr. Chem.*, 1912, [ii], 86, 250—256).—The condensation of *d*-3-methyl*cyclo*hexanone and phenyl styryl ketone by means of sodium hydroxide in alcoholic solution yields, in addition to the β-phenyl-β-4-methyl*cyclo*hexan-2-onylpropiophenone (m. p. 149—151°),

$$COPh{\cdot}CH_2{\cdot}CHPh{\cdot}C\!<\!\begin{matrix} CH_2{\cdot}CH_2 \\ CO{-}CH_2 \end{matrix}\!>\!CHMe,$$

previously described (Abstr., 1902, i, 472; 1903, i, 115), a *stereoisomeride* of m. p. 135—137°, which is separated from the former compound by taking advantage of its greater solubility in carbon tetra-

chloride. If the condensation is effected by means of piperidine, β-piperidyl-β-phenylpropiophenone is formed as an intermediate product (compare Georgi and Schwyzer, this vol., i, 787). The diketone of m. p. 149—151° has $[\alpha]_D^{20}$ − 20·12°, gives at first a yellow and then a red coloration with sulphuric acid, and decomposes at 230° under ordinary pressure, yielding 3-methyl*cyclo*hexanone; the *mono-semicarbazone*, $C_{23}H_{27}O_2N_3$, crystallises in white needles, m. p. 202—204° (decomp.), $[\alpha]_D$ + 84·10°; the monoxime has m. p. 215—216°, $[\alpha]_D^{18}$ + 34·22°, and cannot be transformed into a dioxime by the further action of hydroxylamine, but, when warmed with semicarbazide in alcoholic solution, yields an *oxime-semicarbazone*, $C_{23}H_{28}O_2N_2$, crystallising in white needles, m. p. 239° (decomp.), $[\alpha]_D$ + 49·65°. On reduction with hydriodic acid and phosphorus the diketone is converted into a yellow oil, from which crystals, having m. p. 130—132° and consisting of an *anhydride* of 1 : 9-*dihydroxy*-1 : 3-*diphenyl*-7-*methyl-octahydroindene* (formula I) are occasionally deposited. Under the the influence of sodium hydroxide, it condenses with benzaldehyde in alcoholic solution, yielding a *substance*, m. p. 156—157°, together with the *compound*,



(I.)

$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad CH_2{\cdot}CH_2{\cdot}CHMe \\ COPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH{-}CO{-}CH{\cdot}CHPh{\cdot}OH \end{array}$$

The latter compound forms white needles, m. p. 200—201·5°, $[\alpha]_D^{18}$ − 47·45°, and, on distillation, decomposes at 130—180° with the formation of acetophenone.

The stereoisomeric diketone of m. p. 135—137° has $[\alpha]_D^{20}$ + 83·99°, forms a *monoxime*, m. p. 204—205° (decomp.), $[\alpha]_D^{15·5}$ − 86·80°, and is converted by boiling with alcoholic hydroxylamine hydrochloride into 2 : 4-diphenyl-7-methyl-5 : 6 : 7 : 8-tetrahydroquinoline, m. p. 111—113°, $[\alpha]_D$ + 48·55°. All rotations given above refer to chloroform solutions.

F. B.

Two Stereoisomeric Semicyclic 1:5-Diketones from 3-Methyl*cyclo*hexanone and Phenyl Methylenedioxystyryl Ketone. CURT STRIEGLER (*J. pr. Chem.*, 1912, [ii], 86, 257—269).—The condensation of *d*-3-methyl*cyclo*hexanone with phenyl *mp*-methylenedioxystyryl ketone by means of sodium hydroxide, diethylamine, or piperidine in alcoholic solution gives rise to two stereoisomeric β-mp-*methylene-dioxyphenyl*-β-4-*methyl*cyclo*hexan*-2-*onylpropiophenones*,

$$COPh{\cdot}CH_2{\cdot}CH(C_6H_3{:}O_2{:}CH_2){\cdot}CH{<}^{CH_2\cdot CH_2}_{CO-CH_2}{>}CHMe,$$

which are separated by fractional crystallisation from a mixture of ethyl acetate and alcohol. The less soluble modification has m. p. 152—154°, $[\alpha]_D^{17}$ − 19·59° in chloroform solution. Its alcoholic solution (solubility 1 : 520 at 17·5°) gives a yellow coloration with ferric chloride; the *disemicarbazone*, $C_{25}H_{30}O_4N_6$, has m. p. 223—224° (decomp.), and $[\alpha]_D$ + 37·65° in chloroform; the *monoxime* forms needles, m. p. 216—217°, $[\alpha]_D$ − 26·08° in glacial acetic acid solution. It is oxidised by chromium trioxide in glacial acetic acid solution to β-methyladipic and benzoic acids.

The more readily soluble diketone has m. p. 137—139°, $[\alpha]_D^{17}$ + 69·17°

in chloroform solution, solubility in alcohol 1 : 376 at 17·5°, and forms a *disemicarbazone*, m. p. 172—173°, $[\alpha]_D^{17}$ $-30·56°$ in chloroform solution, a *monoxime*, m. p. 183—184°, $[\alpha]_D$ $-16·08°$ in acetone, and a *dioxime*, $C_{28}H_{26}O_4N_2$, crystallising in needles, m. p. 197—199°, $[\alpha]_D$ $-104·90°$ in acetone solution.

On treatment with hydrogen chloride in benzene solution the isomeric monoximes yield the same 2-*phenyl*-4-mp-*methylenedioxyphenyl*-7-*methyl*-5 : 6 : 7 : 8-*tetrahydroquinoline*,

$$\begin{array}{l} C(C_6H_3{:}O_2{:}CH_2){:}C\cdot CH_2\cdot CH_2 \\ CH{:}CPh\cdot N{=\!=\!=}C\cdot CH_2\cdot CHMe, \end{array}$$

which crystallises in leaflets, m. p. 125—126°, $[\alpha]_D$ $+44·66°$ in chloroform, gives an olive-green coloration with sulphuric acid, and may also be obtained by heating the stereoisomeric diketones (1 mol.) with hydroxylamine hydrochloride (3 mols.) in alcoholic solution; the *picrate*, $C_{29}H_{24}O_9N_4$, has m. p. 180—181° (decomp.), $[\alpha]_D$ $-30·14°$ in chloroform.

On reduction with hydriodic acid and phosphorus, or when dissolved in alcohol and the solution treated simultaneously with carbon dioxide and sodium amalgam, the diketones yield two stereoisomeric 1 : 9-*dihydroxy*-1-*phenyl*-3-mp-*methylenedioxyphenyl*-7-*methyloctahydroindenes*,

$$\begin{array}{l} CH(C_6H_3{:}O_2{:}CH_2)\cdot CH\cdot CH_2 — CH_2 \\ CH_2\cdot CPh(OH) — C(OH)\cdot CH_2\cdot CHMe, \end{array}$$

of which the one modification, obtained from the diketone of m. p. 152—154°, crystallises in white needles, m. p. 66—68°, and has $[\alpha]_D$ $-3·82°$ in chloroform, whilst the stereoisomeride, prepared from the more readily fusible diketone, crystallises in lustrous prisms, m. p. 83—84°, and has $[\alpha]_D$ $-25·35°$ in chloroform; both isomerides give a violet-red coloration with sulphuric acid.

The diketones distil with partial decomposition at about 75°/12 mm., but under ordinary pressure are resolved at 165—175° into methyl*cyclo*hexanone and phenyl *mp*-methylenedioxystyryl ketone. When heated either alone or in high boiling solvents, they undergo no racemisation.

6-*Piperonylidene*-3-*methyl*cyclo*hexanone*,

$$CHMe{<}\begin{smallmatrix} CH_2\cdot CH_2 \\ CH_2 — CO \end{smallmatrix}{>}C{:}CH\cdot C_6H_3{:}O_2{:}CH_2,$$

prepared by the condensation of *d*-3-methyl*cyclo*hexanone and piperonaldehyde by means of alcoholic sodium ethoxide at a low temperature, crystallises in pale yellow needles, m. p. 85°, $[\alpha]_D$ $-227·48°$ in alcoholic solution.

2 : 6-*Dipiperonylidene*-3-*methyl*cyclo*hexanone*,

$$\begin{array}{l} CH_2{:}O_2{:}C_6H_3\cdot CH{:}C — CO — C{:}CH\cdot C_6H_3{:}O_2{:}CH_2, \\ \qquad\qquad\qquad\quad CHMe\cdot CH_2\cdot CH_2 \end{array}$$

prepared from excess of piperonaldehyde in a similar manner, is orange-yellow, and has $[\alpha]_D$ $-31·62°$ in alcohol. F. B.

Semicyclic 1 : 5-Diketones Prepared by the Addition of 3-Methyl*cyclo*hexanone to Phenyl *p*-Methoxystyryl Ketone and Distyryl Ketone. GEORGE S. CRUIKSHANKS (*J. pr. Chem.*, 1912, [ii], 86, 269—272).—Under the influence of sodium hydroxide,

d-3-methyl*cyclo*hexanone condenses with phenyl *p*-methoxystyryl ketone in alcoholic solution, yielding two stereoisomeric β-p-*methoxyphenyl*-β-4-*methyl*cyclo*hexan*-2-*onylpropiophenones*,

$$COPh\cdot CH_2\cdot CH(C_6H_4\cdot OMe)\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ CO-CH_2\end{matrix}{>}CHMe,$$

which are separated by fractional crystallisation from a mixture of ethyl acetate and light petroleum.

The more readily soluble isomeride has m. p. 128—130°, $[\alpha]_D$ +19·2° in chloroform, and is oxidised by chromium trioxide in glacial acetic acid solution to β-methyladipic and benzoic acids, whilst the less soluble modification has m. p. 157—159°, $[\alpha]_D$ +71·21° in chloroform, and gives a reddish-yellow coloration with sulphuric acid.

[With Alexander Schwyzer.]—When heated with hydroxylamine hydrochloride in alcoholic solution both isomerides are converted into 2-*phenyl*-4-p-*methoxyphenyl*-7-*methyl*-5 : 6 : 7 : 8-*tetrahydroquinoline*,

$$\begin{matrix}CH\cdot C(C_6H_4\cdot OMe){:}C\cdot CH_2\cdot CH_2\\ CPh\cdot N{=\!=\!=\!=\!=\!=}C\cdot CH_2\cdot CHMe\end{matrix},$$

which forms an amorphous, yellow powder, $[\alpha]_D$ +46·35° in chloroform, and yields a *picrate*, $C_{29}H_{26}O_8N_4$, m. p. 170°, $[\alpha]_D$ −45·55° in chloroform, a yellow *platinichloride*, and a dark yellow *dichromate*.

β-4-*Methyl*cyclo*hexan*-2-*onyl*-β-*phenylethyl styryl ketone*,

$$CHPh{:}CH\cdot CO\cdot CH_2\cdot CHPh\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ CO-CH_2\end{matrix}{>}CHMe,$$

prepared by the condensation of distyryl ketone and 3-methyl*cyclo*hexanone by means of diethylamine, has m. p. 149—150°.

F. B.

Bicyclic Ketone–Alcohol Prepared by the Addition of Menthone to Phenyl Styryl Ketone. Hans Stobbe and Arthur Rosenburg (*J. pr. Chem.*, 1912, [ii], 86, 226—232).—The condensation product from menthone and phenyl styryl ketone differs from the compounds (1 : 5-diketones) obtained by the combination of *cyclo*pentanone and 3-methyl*cyclo*hexanone with αβ-unsaturated ketones (compare preceding abstracts) in behaving as a monoketone; thus it forms only a monoxime and a monosemicarbazone, does not condense with aromatic aldehydes, and cannot be converted by the action of hydroxylamine hydrochloride into a tetrahydroquinoline derivative.

The authors imagine that the 1 : 5-diketone,

$$COPh\cdot CH_2\cdot CHPh\cdot C_{10}H_{17}O,$$

first produced, undergoes internal condensation, with the formation of a ketone alcohol:

$$\begin{matrix}CHPh-\!\!-CH-CHMe\\ CH_2 \quad CO \quad CH_2\\ CPh(OH)\cdot CPr^\beta\cdot CH_2\end{matrix} \quad \text{or} \quad \begin{matrix}CHPh-\!\!-CPr^\beta\cdot CH_2\\ CH_2 \quad CO \quad CH_2\\ CPh(OH)\cdot CH-CHMe\end{matrix},$$

but all attempts to obtain evidence of the presence of a hydroxyl group by methylation, acylation, or by the action of phenylcarbimide proved unsuccessful.

4-*Hydroxy*-2 : 4-*diphenyl*-6(or 8)-*methyl*-1(or 5)-iso*propylbic*yclo*nonan*-9-*one* is prepared by the addition of sodium ethoxide to a solution of phenyl styryl ketone in menthone. It crystallises from

alcohol in needles, m. p. 128—129°, $[\alpha]_D$ +57·59° in chloroform, distils almost unchanged under diminished pressure, and gives a light green coloration with sulphuric acid; the *oxime* has m. p. 184—185°, $[\alpha]_D$ +31·89° in chloroform; the *semicarbazone*, m. p. 154—156° with previous sintering, $[\alpha]_D$ +20·13° in chloroform. F. B.

Molecular Rearrangements in the Camphor Series. X. Campholytic Acid and Related Compounds. Walden's Rearrangement. WILLIAM A. NOYES and RALPH S. POTTER (*J. Amer. Chem. Soc.*, 1912, 34, 1067—1080).—Aminodihydrocampholytic acid, $CO_2H\cdot CH<\begin{matrix}CMe_2\cdot CMe\cdot NH_2\\ CH_2-CH_2\end{matrix}$, on distillation by itself or mixed with lime yields the *anhydride*, $C_8H_{14}<\begin{matrix}CO\\ NH\end{matrix}$, $[\alpha]_D^{30}$ 72·8° (in light petroleum); the anhydride can also be obtained by warming the acid with acetic anhydride, but it is then accompanied by *acetylaminodihydrocampholytic acid*, $C_8H_{14}<\begin{matrix}CO_2H\\ NHAc\end{matrix}$, m. p. 218°. By the action of nitrous acid the anhydride is converted into the *nitroso*-derivative, $C_8H_{14}<\begin{matrix}CO\\ N\cdot NO\end{matrix}$, needles, m. p. 188—189° (rapid heating), which on heating with sodium hydroxide solution gives trans-*hydroxydihydrocampholytic acid*, $C_8H_{14}<\begin{matrix}CO_2H\\ OH\end{matrix}$, m. p 133·7°, $[\alpha]_D$ +70·1° (in ethyl acetate), together with smaller quantities of campholytic acid, $C_8H_{13}\cdot CO_2H$, campholytolactone, $C_8H_{14}<\begin{matrix}CO\\ O\end{matrix}$, and *iso*laurolene, $CH_2<\begin{matrix}CH{=}CMe\\ CH_2\cdot CMe_2\end{matrix}$. The same four products can be obtained by the direct decomposition of aminodihydrocampholytic acid with nitrous acid. Distillation of the *trans*-hydroxydihydrocampholytic acid or heating with water causes partial decomposition into campholytic acid, *iso*laurolene, and campholytolactone; to obtain *trans*-hydroxydihydrocampholytolactone it is necessary to heat the acid with acetic anhydride, when the product has m. p. 115—117°, $[\alpha]_D^{27}$ +121·9° (in alcohol). Campholytolactone (Tiemann and Kerschbaum, Abstr., 1901, i, 5), although of almost the same m. p. (118—119°), has $[\alpha]_D$ +8·5° (in alcohol), and gives *cis*-hydroxydihydrocampholytic acid, m. p. 118·5°, $[\alpha]_D$ +50·8° (in alcohol), on treatment with sodium hydroxide solution, whereas the above lactone is reconverted into the *trans*-acid. As both the *cis*- and *trans*-acids are hydrolysed by dilute sulphuric acid to *iso*campholytic acid (otherwise β-campholytic acid), $CO_2H\cdot C<\begin{matrix}CMe\cdot CMe_2\\ CH_2-CH_2\end{matrix}$, and as the resistance to oxidation indicates a tertiary hydroxyl in each, the two acids are probably stereoisomerides; this view is supported by the relative conductivities of the acids (*trans*-acid, k 8·1 × 10^{-6}; *cis*-acid, k 35·8 × 10^{-6}). If this view of their structure is correct, a Walden inversion must occur in the decomposition of aminodihydrocampholytic acid by nitrous acid.

l-Campholytic acid could not be obtained of higher optical activity

than $[\alpha]_D^{30}$ $-74\cdot3°$ (in light petroleum); it has a slightly greater conductivity (k $9\cdot8 \times 10^{-6}$) than *iso*campholytic acid (k $8\cdot0 \times 10^{-6}$).

d-Iododihydrocampholytic acid can be prepared by the action of hydrogen iodide on a solution of *l*-campholytic acid in light petroleum, or on *cis*- and *trans*-hydroxydihydrocampholytic acids in carbon disulphide. The products in the three cases were apparently identical, treatment with sodium hydrogen carbonate yielding campholytic acid, *trans*-hydroxydihydrocampholytic acid, and campholytolactone, whilst reduction with zinc dust and dilute sulphuric acid gave dihydrocampholytic acid, an oily liquid, D^{20} 0·9915, $[\alpha]_D^{25}$ $+34\cdot6°$; *amide*, plates, m. p. 86·5°, $[\alpha]_D^{21}$ $+20\cdot7°$ (in light petroleum). Here, again, therefore, a rearrangement similar to that of Walden must have occurred.

The theoretical portion of the paper includes suggestions as to the mechanism of the Walden inversion. D. F. T.

Attempts to Combine *d*-Fenchone or Camphor with Phenyl Styryl Ketone and Other αβ-Unsaturated Ketones. ROBERT GEORGI and ALEXANDER SCHWYZER (*J. pr. Chem.*, 1912, [ii], 86, 273—276).—A record of unsuccessful attempts to condense *d*-fenchone and camphor with phenyl styryl ketone, benzylideneacetylacetone, and phenyl *p*-methoxystyryl ketone. An alcoholic solution of *d*-fenchone and phenyl styryl ketone, on treatment with aqueous sodium hydroxide, yields the α-modification of dibenzylidenetriacetophenone (Kostanecki and Tambor, Abstr., 1896, i, 557); the latter compound was also obtained by the action of piperidine, diethylamine, or sodium hydroxide on a mixture of camphor and phenyl styryl ketone in alcoholic or benzene solution.

Attempts to condense fenchone with phenyl styryl ketone by means of piperidine gave *β-phenyl-β-piperidylpropiophenone*,

$$C_5H_{10}N\cdot CHPh\cdot CH_2\cdot COPh,$$

which forms a *hydrochloride*, m. p. 123—124°, a *picrate*, m. p. 86—88°, and is resolved by heating either alone or with water into piperidine and phenyl styryl ketone.

The interaction of fenchone, benzylideneacetylacetone, and piperidine yielded benzylidenediacetylacetone (Knoevenagel, Abstr., 1895, i, 50).

F. B.

Action of Sulphuric Acid on Borneol. P. G. GOLUBEFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1061—1067).—The action of sulphuric acid on borneol yields *borneol ether*, $(C_{10}H_{17})_2O$, which is a pale yellow syrup, b. p. 312—314°, $[\alpha]_D$ $-88\cdot56°$, D_0^{18} 0·960, n_D^{24} 1·494, volatilising at 110°. The ether is unchanged by 2% sulphuric acid solution at 170°, and is converted into camphor, $[\alpha]_D$ $+29\cdot27°$, by concentrated nitric acid, and into camphene hydrochloride, m. p. 147°, by hydrochloric acid. It is isomeric with the solid ether obtained by Bouchardat and Lafont (Abstr., 1894, i, 612).

Besides the ether, the action of sulphuric acid on borneol gives camphene, m. p. 48—49°, b. p. 157—160°, which is very similar to the natural camphene from the ethereal oil of the Siberian fir (Abstr., 1909, i, 943), but is optically inactive. T. H. P.

Action of Methyl Iodide and Magnesium on Menthone. IVAN VANIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1068—1075).—3-*Methylmenthan*-3-*ol* (1 : 3-*dimethyl*-6-iso*propyl*cyclo*hexan*-1-*ol*),

$$CHMe<\begin{matrix}CH_2\cdot CMe(OH)\\CH_2\text{———}CH_2\end{matrix}>CHPr^{\beta},$$

prepared by the action of magnesium and methyl iodide on menthone, is a liquid, b. p. 102—103°/16—17 mm., D_0^0 0·9143, D_0^{20} 0·8980, and has the normal molecular weight in boiling benzene. The corresponding chloro-derivative, $C_{11}H_{21}Cl$, b. p. about 101—103°/13 mm., could not be obtained pure.

When heated with potassium hydrogen sulphate, the alcohol is converted into the *hydrocarbon*, $CHMe<\begin{matrix}CH_2\cdot CMe\\CH_2-CH_2\end{matrix}>CHPr^{\beta}$ or

$$CHMe<\begin{matrix}CH{=}CMe\\CH_2\cdot CH_2\end{matrix}>CHPr^{\beta},$$

which is a colourless liquid, b. p. 185—187°/764·4 mm., D_0^0 0·8432, D_0^{20} 0·8244, and has the normal molecular weight in boiling benzene. The hydrocarbon combines with 1 mol. of bromine, but the product loses 1 mol. of hydrogen bromide, giving the *compound*, $C_{11}H_{19}Br$, as a dense oil. T. H. P.

The Ethereal Oils of the Wood of the Spruce. PETER KLASON and B. SEGERFELT (*Arkiv. Kem. Min. Geol.*, 1912, **4**, No. 20, 1—3).—In the manufacture of spirit by the sulphite-cellulose process, it has been noticed that a reddish-brown oil, possessing a peculiar odour, collects in the middle of the fractionating tower. When this oil is distilled in a current of steam, a white substance possessing an odour similar to that of camphor collects in the condenser. It has a composition corresponding with the formula $C_{10}H_{17}\cdot OH$, and has m. p. 207°. It begins to sublime at 190° and is optically inactive. The properties point to it being borneol, but whether it is a mixture of borneol and *iso*borneol awaits further investigation. No definite conclusions can yet be drawn as to the condition in which the borneol existed in the original spruce wood, since it would probably be affected by the fermentation process. It was possibly present as bornyl acetate, which was saponified during the boiling with sulphite. T. S. P.

The Formation of Resin by the Action of Alkali Hydroxides on Aliphatic Aldehydes. I. THOR EKECRANTZ (*Arkiv. Kem. Min. Geol.*, 1912, **4**, No. 27, 1—34).—The present paper deals chiefly with the investigation of the products formed by the action of weak (3%) sodium hydroxide on acetaldehyde at low temperatures, and of the resin formed by the action of concentrated alcoholic sodium hydroxide (10%) on acetaldehyde. The method of preparation of the resin was similar to that adopted by Ciamician (Abstr., 1881, 247), care being taken to keep the temperature down and so prevent the formation of compounds of very high molecular weight. The action of the weak sodium hydroxide was studied in order to obtain, if possible, compounds intermediate in composition between the aldehyde and the resin.

By precipitation with ether from acetone solution the resin was

separated into two chief components, which are isomerides having the formulæ $C_{24}H_{36}O_6$, and denoted as *a*- and *β*-aldehyde-resin. They are probably formed by the condensation of 12 molecules of acetaldehyde with loss of $6H_2O$. The *a*-compound is completely soluble in benzene, whilst the *β*-compound leaves a residue. They do not contain aldehydic, ketonic, hydroxylic or carboxylic groups, nor do they possess the characteristics of esters. By treatment with chlorine and bromine the following compounds were obtained: (*a*) $C_{24}H_{36}O_6Cl_4$, white substance, m. p. 160° (decomp.); $C_{24}H_{36}O_6Br_4$, yellow precipitate, which decomposes at 270° without melting. (*β*) $C_{24}H_{36}O_6Cl_4$, light yellow precipitate, m. p. 220—230°; $C_{24}H_{36}O_6Br_4$, yellowish-grey precipitate, which decomposes on heating without undergoing fusion. The *β*-bromo-compound differs from the others in that it is insoluble in the ordinary solvents.

By treatment of the resin with sulphuric or hydrochloric acids, humus-like substances are readily obtained, which fact points to a constitution similar to that of certain of the carbohydrates.

By oxidation of the *β*-compound with 30% hydrogen peroxide in glacial acetic acid solution, a white, amorphous acid was obtained, having the composition $C_{18}H_{24}O_8$, and m. p. 185°. The corresponding *a*-acid could not be obtained pure.

The products obtained by the action of 3% sodium hydroxide on acetaldehyde appear te be intermediate in composition between crotonaldehyde and aldehyde-resin, and are being further investigated, as also are the products of dry distillation of the resin with calcium oxide and with infusorial earth. T. S. P.

[Structure of Polymerised Vinyl Bromide and Caoutchouc.] NICOLAI N. LJUBAVIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 906—907).—In Ostromisslensky's paper on this subject (this vol., i, 280), no mention is made of the work of Lwoff published in the *J. Russ. Phys. Chem. Soc.* in 1878 and 1880. T. H. P.

The So-called "Insoluble" Constituent of Caoutchouc and its Influence on the Quality. CLAYTON BEADLE and HENRY P. STEVENS (*Zeitsch. Chem. Ind. Kolloide,* 1912, **11**, 61—65).—Observations have been made in reference to the influence of different factors (rolling, smoking, etc.) on the separation of the protein constituents of caoutchouc when plantation rubber is treated with "benzine." So far as the composition of the insoluble constituent is concerned, there appears to be essential difference between the products obtained from "fine para" and from plantation caoutchouc.

Elasticity tests with vulcanised products indicate that the protein constituent has an important influence on the properties of the caoutchouc, and it appears to behave much in the same way as antimony sulphide, that is, as a sulphur carrier. Since artificial rubber does not contain the protein constituent, there will necessarily be a difference in quality as compared with the natural substance.

H. M. D.

Synthesis of Alkylglucosides by the Action of Emulsin. β-Butylglucoside, β-*iso*Butylglucoside, β-Allylglucoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 155, 437—439; *J. Pharm. Chim.*, 1912, [vii], 6, 193—199).—The glucosides were prepared by the general method described already (this vol., i, 672).

β-*Butylglucoside* crystallises in colourless, odourless, very hygroscopic needles, has $[\alpha]_D$ $-35\cdot4°$ in water, is bitter to the taste, very soluble in water or alcohol, and moderately so in ethyl acetate. β-iso-*Butylglucoside*, m. p. 99—100°, resembles its isomeride, but is not hygroscopic; it has $[\alpha]_D$ $-34\cdot96°$ in water. β-*Allylglucoside*, m. p. 97°, crystallises in colourless, hygroscopic needles, is less bitter than the foregoing, and has $[\alpha]_D-40\cdot34°$ in water.

All three glucosides were hydrolysed rapidly by emulsin in water. They all reduced alkaline copper solutions slightly, probably owing to the presence of a small amount of dextrose. T. A. H.

New Synthesis of an Alkylglucoside by means of Emulsin. β-Benzylglucoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 155, 523—524*. Compare this vol., i, 592, 672).—Fischer (compare Abstr., 1894, i, 3) obtained, by the action of hydrogen chloride on a mixture of dextrose and benzyl alcohol, a white, amorphous product, which he concluded was a mixture of α- and β-benzylglucosides. β-Benzylglucoside has now been prepared in a crystalline form by the synthesising action of emulsin. A mixture of benzyl alcohol, containing 5% of water (50 c.c.), dextrose (2 grams), and emulsin (0·2 gram), was left, with frequent shaking, for fifty days at 18—24°. The liquid was then filtered and extracted with water. The aqueous extract, after removal by ether of the last traces of benzyl alcohol, was evaporated to dryness under reduced pressure. The dry residue was dissolved in ethyl acetate, and, after remaining twenty-four hours, the solution was decanted and evaporated to a small bulk, from which, on cooling, β-*benzylglucoside* crystallised in needles, m. p. 106°; $[\alpha]_D$ $-49\cdot78°$. It has a bitter taste, is very soluble in water and alcohol, but does not reduce Fehling's solution. In aqueous solution it is almost completely hydrolysed in two days by means of emulsin. W. G.

Picrotoxin. I. JOHANNES SIELISCH (*Annalen*, 1912, 391, 1—22).—Meyer and Bruger have stated that picrotoxin is a complex of two compounds (picrotoxinin and picrotin) in definite but, apparently, not molecular proportions. The foundation of this statement is the estimation of the picrotoxinin by aqueous bromine. The author has examined thoroughly the accuracy of this method, and finds that the amount of picrotoxinin found can be varied at will by as much as 23% by altering the amount of bromine used or the duration of its action.

When a mixture of molecular quantities of picrotoxinin and picrotin is fractionally crystallised from water, the respective fractions have different rotatory powers; however, if the fractions are kept in contact with the mother liquor for two days, they all have approximately the

* and *J. Pharm. Chim.*, 1912, [vii], 6, 298—301.

same rotatory power, which is identical with that of picrotoxin. Similar results are obtained when picrotoxin itself is fractionally crystallised.

The molecular weight of picrotoxin, determined in glacial acetic acid by the cryoscopic method, increases rapidly with the concentration of the solute, and approaches the value 602 required by the formula $C_{30}H_{34}O_{13}$.

The author is of opinion, therefore, that picrotoxin is an easily decomposible compound of picrotin and picrotoxinin in molecular proportions. C. S.

Leuco-bases and Colouring Matters Derived from Diphenylethylene; Oxidation of the Tetramethyl*cyclo*hexylidene Base by Lead Peroxide. PAUL LEMOULT (*Compt. rend.*, 1912, **155**, 355—358).—A reply to Schmidlin and von Escher (this vol., i, 437). Tetramethyldiaminodiphenyl*cyclo*hexylidenemethane,

$$C_6H_{10}{:}C(C_6H_4{\cdot}NMe_2)_2,$$

on oxidation with lead peroxide gives a pure blue colour which dyes tannin-mordanted cotton a deep blue. In aqueous solution the oxidation product gradually loses its colour, giving rise to a *compound*, $C_6H_8{:}C(C_6H_4{\cdot}NMe_2)_2$, which crystallises from alcohol in needles, m. p. 169°. It is colourless or pale green, soluble in mineral acids without coloration, but dissolves in acetic acid to a blue solution. On oxidation with lead peroxide in acetic acid solution, it gives an intense blue colour, which gradually disappears on keeping the aqueous solution, and by precipitation with ammonia another leuco-base is obtained, m. p. 228°, which differs considerably from the leuco-base of malachite-green in its m. p., in the colours it produces, and in the absorption bands it gives with chloranil in alcoholic solution. W. G.

The Chlorophyll Group. XVII. The Spectral Properties of the Two Chlorophyllans. LÉON MARCHLEWSKI (*Biochem. Zeitsch.*, 1912, **43**, 234—239. Compare this vol., i, 285).—The spectral measurements of *allo*chlorophyllan agree well with those of Tsvett, with the exception that the latter found, in addition, a band λ 628—622, and also with those of Willstätter (for "phæophytin component *b*," which the author holds to be *allo*chlorophyllan) with the exception of one band (Marchlewski, λ 496·5—477·5; Willstätter λ 515—491). The spectrum of *neo*chlorophyllan showed also good agreement with the observations of Tsvett and Willstätter, with the exception that the former described a band λ 637—632, which is absent from the pure preparation. S. B. S.

The Nature of the Compound of Iodine and Tannin. MARCEL BECQUET (*Chem. Zentr.*, 1912, i, 1635; from *Bull. Sci. Pharm.*, 1912, **18**, 645—649).—Tannin and iodine are not chemically combined; the tannin serves as a substratum for hydrogen iodide. The preparation may be replaced by freshly prepared solutions of hydriodic acid of known strength. C. H. D.

Methyltannin. JOSEF HERZIG (*Monatsh.*, 1912, 33, 843—852. Compare Herzig and Renner, Abstr., 1909, i, 713).—When 4 grams of methyltannin (tannin methyl ether) are heated with 10 c.c. of a 7·4% solution of potassium hydroxide in alcohol, the residue obtained on evaporation, after dissolving in water, gives an ether extract containing the ethyl ester of trimethylgallic acid, m. p. 52—55°. The aqueous solution, after extraction with ether, contains a mixture of tri- and di-methylgallic acids, which can be isolated by acidifying and again extracting with ether; the aqueous solution still contained a substance of reducing properties. The above ethyl ester can also be obtained (m. p. 53—55°) by a similar treatment of the corresponding methyl ester with a small amount of potassium hydroxide in ethyl alcoholic solution. If methyltannin is treated in solution in methyl alcohol with an insufficient amount of barium hydroxide, the product is the methyl ester of trimethylgallic acid.

That the results obtained above do not depend on the presence of methyl trimethylgallate as an impurity in the methyltannin is shown by the latter, after repeated recrystallisation from large quantities of alcohol, having an unaltered methoxyl content, and still exhibiting the same behaviour with alcoholic potassium hydroxide. Also, sublimation of methyltannin in an atmosphere of carbon dioxide gave as the only definite products, trimethylgallic acid (m. p. 166—168°) and a trace of a substance, m. p. 135—145°.

The inconsistency in $[\alpha]_D$ for different specimens of methyltannin (Herzig and Renner, *loc. cit.*) appears to be due to the application of warm acetic acid in their preparation. Boiling with acetic acid raises the optical activity of methyltannin very considerably; the change is in all probability connected with the hydrolytic effect of the acetic acid, which causes complete hydrolysis in a sealed tube at 130—140°. Specimens of methyltannin in the preparation of which the use of acetic acid was avoided gave $[\alpha]_D^{18}$ $+9·5°$ to $+10·7°$.

D. F. T.

The Compounds of Dimethylpyrone with Aluminium Bromide and with Trichloroacetic Acid. WLADIMIR PLOTNIKOFF (*Chem. Zentr.*, 1912, i, 1839; from Reprint, 1911).—A *compound*, $AlBr_3,C_7H_8O_2$, is obtained in cold ethylene bromide solution, and has m. p. 120—123°. The freezing-point curve of aluminium bromide and dimethylpyrone indicates the existence of this compound, and of another, $AlBr_3,2C_7H_8O_2$.

A similar freezing-point curve, with two maxima and three eutectic points, indicates the existence of two *compounds* with trichloroacetic acid, $C_7H_8O_2,CCl_3{\cdot}CO_2H$ and $C_7H_8O_2,2CCl_3{\cdot}CO_2H$. A third compound, $2C_7H_8O_2,CCl_3{\cdot}CO_2H$, may also exist. C. H. D.

Constitution of the Phthaleins and Their Derivatives. BERNARDO ODDO and ETTORE VASSALLO (*Gazzetta*, 1912, 42, ii, 204—236).—It has been found (Oddo, Abstr., 1911, ii, 826) that treatment with magnesium ethyl iodide does not reveal the presence of active hydrogen in the phenolphthalein molecule. This result

throws doubt on Baeyer's biphenolic formula:

$$CO<\underset{O}{\overset{C_6H_4}{}}>C<\begin{matrix}C_6H_4\cdot OH\\C_6H_4\cdot OH\end{matrix},$$

since such a compound should yield 2 mols. of ethane, corresponding with the two phenolic hydrogen atoms. Repetition of the above experiment with larger quantities shows that the lactonic group also remains indifferent, whereas in other similar compounds, such as coumarin and santonin, the oxygen of the carbonyl group undergoes replacement by two alkyl groups.

On the other hand, the *monopotassium* salt of phenolphthalein, which has been obtained crystalline in reddish-violet, rhomboidal plates, reacts with magnesium ethyl iodide, giving 1 mol. of hydrocarbon in accord with the dihydroxylic formula $C_{20}H_{13}O_2(OH)\cdot OK$; but here, too, the presence of a lactonic group is not indicated.

Anhydrous ammonia, aniline, dimethylaniline, or pyridine gives no precipitate with an ethereal phenolphthalein solution, and the latter remains colourless. Also, in pyridine solution, phenolphthalein does not react with magnesium ethyl iodide.

Cryoscopic and ebullioscopic measurements give the following results. In freezing phenol, phenolphthalein has the normal molecular weight, even with considerable concentrations. In aniline, however, the molecular weight is only about one-third of the normal value for low concentrations, and only when the concentration exceeds 12% are normal values obtained; Ampola and Rimatori (Abstr., 1897, ii, 306) found that phenols showed normal behaviour in this solvent. In freezing veratrole or dimethylaniline, values agreeing with the simple molecular formula are obtained. In boiling methyl alcohol or acetone, the molecular weight has double the normal value when the concentration is low, and gradually diminishes as this is increased. With pyridine, however, normal ebullioscopic behaviour is shown even at low concentrations.

Unlike phenolphthalein, resorcinolphthalein is found to contain two active hydrogen atoms when treated with magnesium ethyl iodide, this result agreeing with the biphenolic formula; when treated with excess of the reagent, resorcinolphthalein gives, however, no indication of the presence of a lactonic group. Iminophenolphthalein, on the other hand, shows only one active hydrogen atom, although it is usually regarded as possessing the structure:

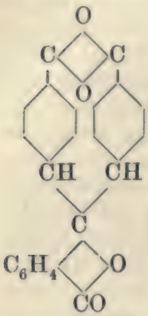
$$CO<\underset{NH}{\overset{C_6H_4}{}}>C<\begin{matrix}C_6H_4\cdot OH\\C_6H_4\cdot OH\end{matrix};$$

its diacetyl and triacetyl derivatives (see below) contain no such hydrogen atoms.

In boiling pyridine, fluorescein shows behaviour different from that of phenolphthalein, molecular weights lower than the theoretical values being obtained at low concentrations. Fluorescein differs from phenolphthalein in combining readily with pyridine in various proportions to form crystalline compounds.

The authors give a brief summary of the results of previous investigations on phenolphthalein and its salts and other derivatives, and discuss these in relation to those given above. The difference

between phenolphthalein and other hydroxylic compounds, such as fluorescein, is to be sought in the different functional disposition of the oxygen atoms usually regarded as hydroxylic. In fluorescein, the two hydroxyl groups are separated by an anhydridic oxygen atom, and their great distance apart and the stability of the triple hexagonal nucleus to which they are attached allows of their existence. With phenolphthalein, however, the hydroxyl groups are in close juxtaposition, and at the same time the benzene nuclei to which they are attached are free; it seems probable, therefore, that the molecule immediately tends to acquire a more stable arrangement, the two oxygen atoms assuming ethereal functions and binding the two benzene nuclei (annexed formula). The monoimino-compound would possess a similar structure.



For the potassium salt, however, must be assumed either the lactophenolic formula, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{-O-}>C<\genfrac{}{}{0pt}{}{C_6H_4\cdot OK}{C_6H_4\cdot OH}$, or the carboxy-quinonoid formula, $CO_2K\cdot C_6H_4\cdot C\leqslant\genfrac{}{}{0pt}{}{C_6H_4\cdot OH}{C_6H_4:O}$, the latter being the more probable.

The results at present obtained with phenolphthalein are also explainable by the formula: $CO<\genfrac{}{}{0pt}{}{C_6H_4}{-O-}>C<\genfrac{}{}{0pt}{}{OPh}{OPh}$.

With pyridine, fluorescein forms yellow, crystalline compounds: (1) $C_{20}H_{12}O_5(C_5H_5N)_2$ and (2) $C_{20}H_{12}O_5(C_5H_5N)_3$, m. p. 95°, which is unstable and is readily transformed into (1).

Triacetylphenolphthaleinimide, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{NAc}>C<\genfrac{}{}{0pt}{}{C_6H_4\cdot OAc}{C_6H_4\cdot OAc}$, forms triclinic [Maddalena] crystals, m. p. 238°. T. H. P.

[Preparation of 14-Chlorocoeramidonine and Allied Compounds.] Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 246337. Compare Abstr., 1906, i, 687; 1907, i, 1067).—14-*Chlorocoeramidonine*, a brownish-yellow powder, is prepared from 4-chlorophenyl-α-aminoanthraquinone by the action of condensing agents; after treatment with sodium hyposulphite it yields a red vat, from which cotton is dyed in clear golden-yellow shades.

12 : 14-*Dichlorocoeramidonine* and *benzocoeramidonine* have similar properties, and are prepared from 2 : 4-dichlorophenyl-α-aminoanthraquinone and α-naphthyl-α-aminoanthraquinone respectively.

14 : 14′-*Coeramidonyl ketone* is obtained by the condensation of di-$\alpha\alpha$-anthraquinonyl-*pp*-diaminobenzophenone, whilst di-$\alpha\alpha$-anthraquinonyl-*o*-tolidine furnishes 14 : 14′-bis-12 : 12′-methylcoeramidonyl.

F. M. G. M.

Substituted Rhodanins and Some of their Aldehyde Condensation Products. XII. Hans Nägele (*Monatsh.*, 1912, 33, 941—965. Compare Abstr., 1910, i, 764).—An extension of the work of Andreasch and Zipser (Abstr., 1903, i, 855).

Phenylrhodanin and *m*-tolualdehyde when heated with a little acetic acid condense to *3-phenyl-5-tolylidenerhodanin*,

$$C_6H_4Me\cdot CH:C<\begin{matrix}S-CS\\ \vert\\ CO\cdot NPh\end{matrix},$$

yellow crystals, m. p. 200°.

3-*Phenyl-5-cuminylidenerhodanin*, obtained in an analogous manner from cuminaldehyde, forms dark yellow crystals, m. p. 204°.

3-iso*Butylrhodanin*, obtained by the action of ethyl chloroacetate on potassium *iso*butyldithiocarbamate, is an unpleasant smelling oil, b. p. 160°/11—12 mm.

5-*Benzylidene*-3-iso*butylrhodanin*, from the previous substance with benzaldehyde, forms yellow leaflets, m. p. 117°.

5-o-*Hydroxybenzylidene*-3-iso*butylrhodanin*, obtained analogously with salicylaldehyde, forms deep yellow needles, m. p. 184°. The isomeric 5-p-*hydroxybenzylidene*-3-iso*butylrhodanin* is a yellow, crystalline powder, m. p. 153°.

5-p-*Methoxybenzylidene*-3-iso*butylrhodanin*, from anisaldehyde, forms yellow crystals, m. p. 115°.

5-p-*Dimethylaminobenzylidene*-3-iso*butylrhodanin*, from dimethylaminobenzaldehyde, is a red, crystalline powder, m. p. 156°.

5-*Piperonylidene*-3-iso*butylrhodanin*, from piperonal, forms yellow crystals, m. p. 122°.

Potassium *iso*butyldithiocarbamate can be converted into *iso*butyl thiocarbimide (compare Kaluza, this vol., i, 440), which reacts with ammonia, forming *iso*butylthiocarbimide; cyanogen acts on an alcoholic solution of this substance, forming a solution of an intermediate product, $CS<\begin{matrix}N(C_4H_9)\cdot C:NH\\ \vert\\ NH——C:NH\end{matrix}$, which is easily hydrolysed by hydrochloric acid to iso*butylthioparabanic acid*; this is desulphurised by silver nitrate solution to iso*butylparabanic acid*, $C_4H_9\cdot N<\begin{matrix}CO\cdot CO\\ \vert\\ CO\cdot NH\end{matrix}$, scales, m. p. 125°.

3 : 3′-*Ethylenedirhodanin*, $\begin{matrix}S——CS\\ \vert\\ CH_2\cdot CO\end{matrix}>N\cdot C_2H_4\cdot N<\begin{matrix}CS-S\\ \vert\\ CO\cdot CH_2\end{matrix}$, m. p. 194°, is prepared from ethylenediamine through the dithiocarbamate in the same way as the corresponding *iso*butyl compound above; its formula was confirmed by analysis and molecular-weight determination in benzene. It condenses with aldehydes in the same way as the simpler rhodanins, but with rather more difficulty.

5 : 5′-*Dibenzylidene*-3 : 3′-*ethylenedirhodanin* forms deep yellow crystals, m. p. 265°.

5 : 5′-*Di*-p-*hydroxybenzylidene*-3 : 3′-*ethylenedirhodanin* chars without melting.

5 : 5′-*Di*-m-*nitrobenzylidene*-3 : 3′-*ethylenedirhodanin* forms pale yellow crystals, m. p. 258° (decomp.).

5 : 5′-*Di*-p-*dimethylaminobenzylidene*-3 : 3′-*ethylenedirhodanin* is a red substance, m. p. 212°.

5 : 5′-*Di*-p-*methoxybenzylidene*-3 : 3′-*ethylenedirhodanin* is a dark yellow, crystalline powder, m. p. 262° (decomp.).

5 : 5′-*Di*-p-*hydroxy*-m-*methoxybenzylidene*-3 : 3′-*ethylenedirhodanin*, formed from vanillin, is a yellow, crystalline powder, m. p. 270° (decomp.).

5 : 5′-*Dicinnamylidene*-3 : 3′-*ethylenedirhodanin* is a deep yellow powder, decomposing at 210°, m. p. 235°.

Ethylenediamine reacts with ethylthiocarbimide, forming diethylethylenethiocarbamide, $(NHEt\cdot CS\cdot NH)_2C_2H_4$, colourless prisms and needles, m. p. 132°, which is converted by cyanogen into a brown, crystalline imino-compound, $\begin{matrix}C(:NH)\cdot C(:NH) \\ \vert \qquad\qquad \\ NEt \text{———————} CS\end{matrix}\!\!>N\cdot C_2H_4\cdot N<\!\!\begin{matrix}C(:NH)\cdot C:NH \\ \qquad\qquad \vert \\ CS \text{————} NEt\end{matrix}$; this on evaporation with hydrochloric acid yields *diethylethylenedithiodiparabanic acid*, pale yellow crystals, which decompose without melting; silver nitrate desulphurises the last substance in alcoholic solution to *diethylethylenediparabanic acid*, colourless crystals, m. p. 168°.

Diallylethylenedithiodiparabanic acid, yellow scales, m. p. 175°, is obtained in the same manner as the diethyl compound above, starting with allylthiocarbimide, and is convertible into *diallylethylenediparabanic acid*, colourless leaflets, m. p. 182°. This and all the above parabanic acids on treatment in aqueous solution with calcium chloride and ammonia deposit calcium oxalate.

Diethylethylenedithiodihydantoin, colourless needles, m. p. 184°, of which the molecular structure is uncertain, is obtained when diethylethylenedithiocarbamide is heated in aqueous solution with chloroacetic acid.

D. F. T.

Alkaloids of Pareira Root. FRANZ FALTIS (*Monatsh.*, 1912, 33, 873—897).—Commercial *Bebirinium sulphuricum* has been examined as to its constituents (compare Scholtz, Abstr., 1911, i, 913; 1907, i, 79, etc.); three have been isolated: β-bebeerine, *iso*bebeerine, and bebeerine-*B*, full details of the method being given.

β-Bebeerine $C_{21}H_{23}O_4N$, the chief constituent (termed β- in order to distinguish it from the very optically active chief constituent obtained by Scholtz), has m. p. 142—150°, $[\alpha]_D^{21}$ (in alcohol) + 28·6°, (in pyridine) − 24·7°; the base and its salts are amorphous; the *iodide* decomposes at 245°. Its chemical behaviour indicates the groups

$$C_{19}H_{16}O_2\cdot NMe(OH)\cdot OMe;$$

the *acetyl* derivative, m. p. 120—142°, can be further converted into a *triacetyl* compound, m. p. 140—165°, one acetyl group entering the nucleus. Benzoylation also yields a red *tribenzoyl* derivative, m. p. 144—147°. Methylation by nitrosomethylcarbamide gives a methyl derivative, needles, m. p. 81—83°; the action of methyl sulphate aided by heat causes methylation at the nitrogen atom, the quaternary *iodide*, $C_{19}H_{16}O_2(NMe_2I)(OH)\cdot OMe$, obtained from the reaction product being soluble in alkali; treatment with methyl sulphate at 0° (compare Pschorr, Abstr., 1911, i, 908) methylates only the hydroxyl group, the *hydriodide* of the product, $C_{19}H_{16}O_2NMe(OMe)_2$, having m. p. 244° (decomp.), and containing two molecules of water of crystallisation.

In an experiment in which β-bebeerine was boiled with benzene, some unknown impurity in the latter caused a conversion into an insoluble optically inactive product; endeavours to repeat the necessary conditions failed. The inactive compound is a *tertiary base*,

yielding a *methiodide*, decomposing at 245°; under the influence of hydrogen iodide the base is converted into a quaternary *iodide*, m. p. 250° (decomp.), the base of which contains the elements of two molecules of bebeerine, together with those of a molecule of water. It is uncertain whether the coupling of the molecules occurred before or after the treatment with hydrogen iodide.

The alkaloid *B* is a yellow powder, m. p. 220° (decomp), $[\alpha]_D + 56{\cdot}7°$ (in pyridine). Fusion with potassium hydroxide causes the formation of protocatechuic acid, and investigation of the groups indicates a formula $C_{20}H_{15}O_2(NMe)(OH)_2{\cdot}OMe$.

*iso*Bebeerine, $C_{19}H_{15}O(NMe)(OH)_2{\cdot}OMe$, forms rhombic needles, m. p. 290° (decomp.); it is optically inactive.

It is suggested that the bebeerine (α-bebeerine) obtained by Scholtz (*loc. cit.*) was really of the same composition as the β-bebeerine above, and actually a stereoisomeride. D. F. T.

The Constituents of Buphane disticha. FRANK TUTIN (*Arch. expt. Path. Pharm.*, 1912, **69**, 314).—Lewin (this vol., i, 577) has recently described the isolation of an alkaloid from *Buphane disticha*, for which he proposes the name "hæmanthine." The author points out that he has previously published an investigation on the same material (Trans., 1911, **99**, 1240), and shown that it contains at least four alkaloids. Probably, hæmanthine is a mixture of at least two alkaloids, buphanine being the main constituent. H. W.

Hydrogenated Derivatives of *apo*Harmine. VICTOR HASENFRATZ (*Compt. rend.*, 1912, **155**, 284—286. Compare this vol., i, 577).—Fischer (Abstr., 1889, 730) prepared dihydro*apo*harmine by reduction of *apo*harmine with phosphorus and hydriodic acid. The author has repeated the process and obtained, in addition, *tetrahydro*apo*harmine*, $C_8H_{12}N_2,H_2O$, which crystallises from water in long, colourless, flattened needles, m. p. 96°. It is readily soluble in hot water, sparingly so in cold, and gives a *picrate*, very soluble in cold water.

Dihydro*apo*harmine gives a *methiodide*, which is not decomposed by boiling aqueous potassium hydroxide. The existence of methyl*apo*harmine and nitrosodihydro*apo*harmine shows the presence of an :NH group in *apo*harmine and its dihydro-derivative. Since, however, the methiodide of the latter, unlike that of the former, is not decomposed by potassium hydroxide, the methyl iodide in the latter must be attached to a tertiary amino-group; thus dihydro*apo*harmine is both a secondary and a tertiary base, and this also applies to *apo*harmine, harmine and harmaline, the alkaloids of *Peganum harmala*. W. G.

Ethylmorphine and Ethylmorphine Hydrochloride (Dionine). GEORGE L. SCHAEFER (*Amer. J. Pharm.*, 1912, **84**, 389—391).—The figures published for the m. p.'s and solubilities of ethylmorphine and ethylmorphine hydrochloride are very discordant. The author has prepared pure ethylmorphine and finds that it has no distinct m. p., but begins to soften at about 88°, becomes transparent at 90—91°, and slowly liquefies at 110—115°. Its solubility is 1 : 480 in water, 1 : 75 in ether, and 1 : 1·5 in alcohol at 25°. The hydrochloride, also, has no

definite m. p., but softens at 110°, becomes translucent at about 120°, and liquefies, with decomposition, at a higher temperature. Solubility determinations yielded the following results:

15°	1 : 11·5 in water	1 : 26 in alcohol
25	1 : 8 ,,	1 : 20 ,,
40	1 : 4 ,,	1 : 8·25 ,,
50	1 : 2·5 ,,	1 : 5 ,,

The following test is proposed for ascertaining the purity of ethylmorphine hydrochloride: 2 c.c. of a solution of the specimen in water (1 : 40) at 25° are treated with 3 drops of ammonia (10%). If the salt is pure, the solution remains clear, and soon deposits distinct needle-shaped crystals of ethylmorphine. If the salt is not pure, and amorphous by-products are present, the solution becomes milky, and the separation of crystals may be retarded for hours, according to the amount of amorphous material contained in the preparation.

Salts of ethylmorphine may easily be distinguished from those of methylmorphine by dissolving 0·05 gram of the specimen in water (5 c.c.) and adding 5 drops of ammonia (10%). If allowed to remain for about two hours, ethylmorphine will separate, whilst a solution of methylmorphine remains clear, without separating crystals.

H. W.

Preparation of Compounds from Alkylarylbarbituric Acids and Cinchona Alkaloids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247188).—When the cinchona alkaloids are treated at the ordinary temperature with equimolecular proportions of alkylarylbarbituric acids in alcoholic or aqueous-alcoholic solution they furnish crystalline compounds of therapeutic value. The *compounds* from phenylethylbarbituric acid with quinine and with hydroquinine ($C_{20}H_{26}O_2N_2,2H_2O$) have m. p.'s 182—183° and 165° respectively.

F. M. G. M.

Solanidine from Solanum tuberosum II. AMEDEO COLOMBANO (*Gazzetta*, 1912, **42**, ii, 101—116. Compare Abstr., 1908, i, 99).—The author has prepared solanidine from *Solanum tuberosum* in three different ways, the three products having the same crystalline characters and melting point, 214—215°. Analysis leads to the formula $C_{25}H_{39}ON$, which, however, requires confirmation.

Solanidine from *Solanum tuberosum* differs from solanidine from *S. sodomaeum*, not only as regards its m. p., but also in its behaviour towards bromine. The latter does not decolorise aqueous or chloroform solutions of bromine, whilst the former combines with bromine, giving a moderately stable compound, m. p. 103—108° (decomp.), which is rich in bromine, but has not yet been analysed.

Solanidine from *S. tuberosum* yields a camphorsulphonate (from Reychler's camphorsulphonic acid: Abstr., 1899, i, 445), forming tufts of crystals, m. p. 170—180°, and a bromocamphorsulphonate, m. p. 160—180°. These salts have not yet been analysed. T. H. P.

Strychnine and Brucine. RICCARDO CIUSA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 84—87. Compare Abstr., 1911, i, 155, 1016).—The action of bromine on *iso*strychnine gives a *compound*

which crystallises from alcohol in colourless prisms of the composition $CO_2Et\cdot C_{20}H_{22}NBr_3\dot{:}NH,HBr$, 1 mol. of bromine being added to the molecule and a further atom introduced in place of a hydroxyl group of the *iso*strychnine. Crystallisation from pyridine in place of alcohol yields the *pyridine* salt, $CO_2H\cdot C_{20}H_{21}NBr_3\dot{:}NH,C_5H_5N$, which has a curarine action greater than that of *iso*strychnine, whilst the strychnine action has completely disappeared T. H. P.

Compounds of Cupric Thiosulphate with Various Amines. G. Rossi (*Gazzetta*, 1912, 42, ii, 185—188).—The final product of the interaction of a cupric salt with sodium thiosulphate consists of cuprous thiosulphate, which, according to the conditions, crystallises either alone or combined with sodium thiosulphate. That cupric thiosulphate is formed as an intermediate product of the reaction is shown by the fact that the simultaneous presence of pyridine results in the separation of blue crystals of the compound

$$CuS_2O_3,4C_5H_5N,6H_2O.$$

Similarly, with aniline, CuS_2O_3,NH_2Ph, and with hexamethylenetetramine, $CuS_2O_3,C_6H_{12}N_4,4H_2O$, are formed. T. H. P.

Preparation of Glycocyamidine. Ernst Schmidt (*Zeitsch. Allg. Oesterr. Apothekervereins*, 1912, reprint 3 pp.).—Whilst creatine is readily converted into creatinine by repeated evaporation with concentrated hydrochloric acid, its homologue, glycocyamine, only yields small quantities of glycocyamidine when heated with the same reagent. When, however, glycocyamine is warmed on the water-bath during twenty-four hours with concentrated sulphuric acid, a good yield of glycocyamidine hydrochloride, darkening at 200°, m. p. 208—210° (decomp.), is obtained. H. W.

Purines. VII. 2-Oxy-6 : 8 : 9-trimethylpurine, 2-Oxy-6 : 9-dimethylpurine, and 2-Oxy-8 : 9-dimethylpurine. Carl O. Johns (*J. Biol. Chem.*, 1912, 12, 91—96).—None of the many isomerides of the monoxytrimethyl purines has yet been described, and if they occur in the cleavage of nuclein they might easily be overlooked, since they would probably be readily soluble in water.

2-*Oxy*-6 : 8 : 9-*trimethylpurine* is rather soluble in water, in spite of the fact that two of the three methyl groups are attached to carbon atoms. It was prepared by heating 5-*acetylamino*-6-*methylamino*-4-*methyl*-2-*pyrimidone* (decomp. 290—300°) at 225—230° with acetic anhydride. It contains $2H_2O$ and decomposes at 275°; the *picrate* decomposes at 253°.

2-*Oxy*-6 : 9-*dimethylpurine*, prepared by the action of 85% formic acid on 5-amino-6-methylamino-4-methyl-2-pyrimidone, does not melt at 320°; the *picrate* decomposes at 224°. When 5-amino-6-methylamino-2-pyrimidone is heated with acetic anhydride at 150—160°, a 90% yield of 2-*oxy*-8 : 9-*dimethylpurine* is obtained. This does not melt at 320° and is readily soluble in cold water; its *picrate* decomposes at 233°. W. D. H.

Desmotropism in the ψ-Thiohydantoins. Treat B. Johnson and Joseph A. Ambler (*Amer. Chem. J.*, 1912, 48, 197—205).—An

attempt to throw light on the possible tautomerism of the ψ-thiohydantoins by an investigation of the properties of a salt of ψ-thiohydantoinacetic acid with an active base.

ψ-Thiohydantoinacetic acid, $CO_2H\cdot CH\colon C<\begin{matrix}CO\text{——}NH\\ C(\colon NH)\cdot S\end{matrix}$ (Tambach, Abstr., 1895, i, 13; Andreasch, Abstr., 1896, i. 89), obtained by heating together fumaric acid and thiocarbamide suspended in a little water, has m. p. 245—250°; although it contains an asymmetric carbon atom it has not been resolved into active constituents. The *hydrochloride*, forms prisms, m. p. 210—212° (decomp.); *barium* salt crystallises with one molecule of water of crystallisation; *cinchonine* and *strychnine* salts, extremely soluble in water. The acid is hydrolysed by hydrochloric acid to dioxythiazoleacetic acid.

The *brucine* salt, m. p. 177°, could not be resolved by recrystallisation from water; the aqueous solution shows mutarotation, initial $[\alpha]_D^{20}$ $-12{\cdot}65°$, changing slowly for several days or rapidly on boiling to $[\alpha]_D^{20}$ $-25{\cdot}0°$ to $-25{\cdot}2°$. This alteration is attributed to a desmotropic change in the molecule of the acid. D. F. T.

Reactions of the Isatins. MORITZ KOHN and ARTUR KLEIN (*Monatsh.*, 1912, 33, 929—940).—When isatin is cautiously warmed with acetic anhydride and zinc dust until the mixture becomes decolorised, a colourless substance, monoclinic crystals, m. p. 223°, is obtained. Analysis and molecular-weight determinations indicate a formula $C_{16}H_8O_4N_2Ac_4$, and the substance is probably *tetra-acetylisatide*, possibly previously isolated by Heller (Abstr., 1904, i, 416). The existence of such a derivative favours the old pinacone structure for isatide, and the probable formula for the new compound is

$$NAc<\begin{matrix}C_6H_4\\ CO\end{matrix}>C(OAc)\cdot C(OAc)<\begin{matrix}C_6H_4\\ CO\end{matrix}>NAc.$$

In an analogous manner, 5-bromoisatin reacts with zinc dust and acetic anhydride, producing 5 : 5′-*dibromotetra-acetylisatide*, monoclinic prisms, m. p. 238—242° (decomp.).

Isatin and 2-methylquinoline when heated together at 160—170° undergo condensation to form 3-*quinaldylideneisatin*,

$$NH<\begin{matrix}C_6H_4\\ CO\end{matrix}>C\colon CH\cdot C_9NH_6;$$

it forms orange-red needles, m. p. 234°. 5-Bromoisatin forms an analogous 5-*bromo*-3-*quinaldylideneisatin*, orange-red needles, which decompose at 265—267. Unlike the previous two cases, a mixture of 5 : 7-dibromoisatin and 2-methylquinoline in suspension in boiling amyl alcohol forms an aldol condensation product,

$$NH<\begin{matrix}C_6H_2Br_2\\ CO\end{matrix}>C(OH)\cdot CH_2\cdot C_9NH_6,$$

a colourless *substance*, tablets, decomposing at 205° approx.

1-Methylisatin reacts with phosphorus pentachloride on warming, with the formation of 2-*dichloro*-1-*methylisatin*, needles, m. p. 142—145°; on treatment with barium hydroxide solution this gives 1-methylisatic acid as the *barium* salt, yellow needles; *silver* salt, deep yellow needles. D. F. T.

[**Preparation of Benzoyl-α-isatinanilide.**] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 246715).—*Benzoyl-α-isatinanilide*, yellow crystals, m. p. 258—259°, is prepared by boiling α-isatinanilide (10 parts) with benzoyl chloride (50 parts) until the mixture assumes a yellowish-brown colour, the product (which separates on cooling) is washed with benzoyl chloride, and crystallised from xylene; it forms a colourless, sparingly soluble (in water) *compound* with sodium hydrogen sulphite, and with fuming sulphuric acid furnishes soluble sulphonated derivatives, which dye wool in yellow shades. F. M. G. M.

A Red Compound of Cuprous Iodide with Quinoline Methiodide. MORITZ KOHN (*Monatsh.*, 1912, **33**, 919—922).—An aqueous solution of quinoline methiodide colours cuprous iodide red, due to the formation of a substance which can be prepared more conveniently by the interaction of an aqueous solution of the methiodide and cuprous iodide dissolved in aqueous potassium iodide. The product is a red powder (microscopic needles); it can also be prepared by dissolving cuprous iodide in warm quinoline and treating with methyl iodide at room temperature.

The compound, which can be washed with water without appreciable decomposition, is shown by analysis to have the composition CuI,C_9H_7N,CH_3I. D. F. T.

Doubly-linked Carbon Atoms and the Carbon–Nitrogen Linking. X. Degradation of Quinoline and of *iso*Quinoline by Reduction. HERMANN EMDE (*Annalen*, 1912, **391**, 88—109. Compare Abstr., 1911, i, 718).—1 : 1-Dimethyltetrahydroquinolinium iodide, which is obtained conveniently by mixing tetrahydroquinoline, methyl iodide, methyl alcohol, and sodium methoxide, is stable in aqueous solution towards sodium amalgam. The corresponding chloride, however, is readily attacked in concentrated aqueous solution on the water-bath, yielding o-*propyldimethylaniline*, $NMe_2\cdot C_6H_4Pr$, b. p. 228—229°/733 mm. This base forms a *picrate*, m. p. 99°; *platinichloride*, m. p. 152°, and *methiodide*, m. p. 179°; the *aurichloride*, yellow leaflets, and *platinichloride*, orange-red needles, of the last have m. p. 179° and 223° (decomp.) respectively.

In a similar manner, 2 : 2-dimethyltetrahydro*iso*quinolinium chloride in concentrated aqueous solution is decomposed by sodium amalgam on the water-bath, and yields o-*vinylbenzyldimethylamine*,

$$CH_2{:}CH\cdot C_6H_4\cdot CH_2\cdot NMe_2,$$

b. p. 216—218°/754 mm. The substance, which has not been obtained quite pure by this method, forms a *picrate*, m. p. above 100°, yellow needles; *aurichloride*, m. p. 135°, golden leaflets, and *methiodide*, m. p. 199°, colourless needles (*picrate*, m. p. 154°; *aurichloride*, m. p. 120—140°; *platinichloride*, decomp. 235°). *o*-Vinylbenzyldimethylamine in a purer condition is obtained by the distillation of a concentrated aqueous solution of 2 : 2-dimethyltetrahydro*iso*quinolinium hydroxide; the picrate, aurichloride, and *platinichloride* have m. p. 105°, 165°, and 184° respectively. The methiodide has m. p. 199°, and the picrate,

aurichloride, and platinichloride derived therefrom have m. p. 165° and 171—172°, and decomp. 235° respectively.

It seems, therefore, that in the tetrahydro*iso*quinoline series, Hofmann's method and the author's method yield the same initial fission product. Whilst, however, the further treatment of this product by Hofmann's method does not give satisfactory results, the elimination of the nitrogen from it is readily accomplished by the author's process.

o-Vinylbenzyldimethylamine is converted into its methochloride, an aqueous solution of which is then reduced on the water-bath by 5% sodium amalgam. Trimethylamine is obtained together with o-*methylstyrene*, $CH_2{:}CH{\cdot}C_6H_4Me$, b. p. 168°/746 mm., which readily polymerises to a substance resembling caoutchouc. *o*-Methylstyrene has also been prepared from *o*-xylene as follows: *o*-Xylene is converted successively into *o*-xylyl bromide, *o*-tolylacetonitrile, and *β*-*o*-tolylethylamine, $C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, by the usual methods. The base has b. p. 227°, and forms a *carbamate*,

$$C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO_2{\cdot}NH_3{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4Me,$$

m. p. 111°, *hydrochloride*, $C_9H_{13}N,HCl,3H_2O$, m. p. 78° (227° when anhydrous), *platinichloride*, decomp. about 253°, *picrate*, m. p. 177°, and *aurichloride*, which has different m. p.'s according to the amount of water of crystallisation it contains, but decomposes at about 195°. A methyl-alcoholic solution of the carbamate reacts with methyl iodide and sodium methoxide to form *trimethyl-β-*o*-tolylethylammonium iodide*, $C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I$, m. p. 250°. The corresponding *picrate*, m. p. 152·5°, long, orange-yellow needles, *aurichloride*, m. p. 156°, golden-yellow needles, and *platinichloride*, decomp. 244°, orange needles, are described. By distillation with 33% potassium hydroxide, the iodide is decomposed, and yields trimethylamine and *o*-methylstyrene.

C. S.

Asymmetric Selenites. II. Additive Products of Piperidine with Selenious and Sulphurous Acids. LUIGI MARINO and A. TONINELLI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 98—103. Compare this vol., i, 127).—In boiling methyl alcohol the compound $C_5H_{11}N{\cdot}SeO_2$ appears to be dissociated to some extent, whilst the analogous sulphur derivative, $C_5H_{11}N{\cdot}SO_2$ (compare Michaelis, Abstr., 1895, i, 430), exhibits the normal molecular weight. The specific conductivities of the selenium and sulphur compounds in methyl-alcoholic solutions at 25° are 0·006972 and 0·006303 respectively.

These compounds being good electrolytes, measurements were made with their methyl-alcoholic and aqueous-alcoholic solutions by Bredig and Fraenkel's method (Abstr., 1905, ii, 692) to ascertain if they are acidic in character. The results indicate no interchange of position of the iminic hydrogen to give an acid analogous to aminosulphinic acid.

T. H. P.

Syntheses in the Pyrrole Group. VII. Derivatives of Pyrrole-2- and -3-carboxylic Acids. BERNARDO ODDO and AUGUSTO MOSCHINI (*Gazzetta*, 1912, 42, ii, 244—256. Compare this vol., i, 721).—In the

preparation of pyrrole-2-carboxylic acid by means of magnesium pyrryl iodide (Abstr., 1909, i, 672), a yield of 85% of the acid, calculated on the pyrrole used, is obtainable.

The syntheses of polypeptides may be effected economically and efficiently by treating the amide of pyrrole-2-carboxylic acid with, for example, a chloroacetic ester, chloroacetamide, etc.:

$$C_4NH_4\cdot CO\cdot NH_2 + CH_2Cl\cdot CO_2Et = HCl + C_4NH_4\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$$

(compare Fischer and van Slyke, Abstr., 1911, i, 1020). Further,

$$C_4NH_4\cdot CO\cdot NH_2 + CH_2Cl\cdot CO\cdot NH_2 = HCl + C_4NH_4\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2,$$

and this $+ CH_2Cl\cdot CO_2Et =$

$$HCl + C_4NH_4\cdot CO\cdot NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

the ethyl ester of 2-pyrroylglycylglycine.

In a similar manner, the application of chlorides of carbamic acids, $Cl\cdot CO\cdot NH_2$, and of esters of chloro-formic acid, leads to pyrrole-2-amino-acids of the simplest type, $C_4NH_4\cdot CO\cdot NH\cdot[CO\cdot NH]_n\cdot CO_2H$.

Pyrroyl chloride may be obtained by the action of thionyl chloride on pyrrole-2-carboxylic acid (compare Fischer and van Slyke, *loc. cit.*).

n-*Propyl pyrrole-2-carboxylate*, $C_4NH_4\cdot CO_2Pr$, prepared from magnesium pyrryl bromide and propyl chloroformate, it is a dense, colourless liquid, b. p. 164—167°/50 mm. The iso*butyl* ester, $C_9H_{13}O_2N$, b. p. 119—122°/70 mm., and the iso*amyl* ester, $C_{10}H_{15}O_2N$, b. p. 186—190°/100 mm., are dense, faintly yellow liquids.

The amide of pyrrole-2-carboxylic acid may be obtained, more economically than by Fischer and van Slyke's method (*loc. cit.*), by the action of aqueous ammonia on an ester (methyl) of the acid in a sealed tube (at 155—160°).

By passing a current of carbon dioxide over magnesium pyrryl chloride, heating the mass at 250—270°, and treating with acid, pyrrole-3-carboxylic acid is obtained, the group CO_2MgX migrating from the 2- to the 3-position under the influence of heat. T. H. P.

Syntheses in the Pyrrole Group. VIII. Halogen- and Amino-derivatives of Methylpyrroyl. BERNARDO ODDO and AUGUSTO MOSCHINI (*Gazzetta*, 1912, 42, ii, 257—266. Compare preceding abstract).—2-*Pyrryl chloromethyl ketone*, $C_4H_4N\cdot CO\cdot CH_2Cl$, prepared by the action of chloroacetyl chloride on magnesium pyrryl bromide, forms white needles, m. p. 115°, and exhibits normal cryoscopic behaviour in acetic acid; its *silver* derivative,

$$C_4H_3NAg\cdot CO\cdot CH_2Cl,$$

was prepared. Oxidation of the ketone with permanganate gives 2-pyrrylglyoxylic acid (compare Oddo, Abstr., 1910, i, 426). Under the influence of water or dilute alkali solution, the ketone is converted into 2-pyrryl hydroxymethyl ketone, which readily undergoes resinification.

The action of pyridine on 2-pyrryl chloromethyl ketone yields the *pyridonium* compound, $\begin{matrix}CH\cdot CH\\ \|\\ CH\cdot NH\end{matrix}\!\!>\!C\cdot CO\cdot CH_2\cdot NCl\!<\!\!\begin{matrix}CH\cdot CH\\ CH:CH\end{matrix}\!\!>\!CH$ which forms needles, m. p. 135°, has a distinct alkaline reaction, gives ionic chlorine in aqueous solution, and yields crystalline precipitates

with platinic and auric chlorides. When treated with potassium hydroxide, it yields the corresponding hydroxide (?),

$$C_4NH_4\cdot CO\cdot CH_2\cdot N(OH){:}C_5H_5,$$

m. p. 153° (decomp.).

2-*Pyrryl aminomethyl ketone*, $C_4NH_4\cdot CO\cdot CH_2\cdot NH_2$, forms dark yellow, nacreous leaflets, reduces ammoniacal silver and alkaline copper solutions, and is soluble in dilute hydrochloric acid, from which it is reprecipitated by ammonia.

2-*Pyrryl bromomethyl ketone*, C_6H_6ONBr, forms white needles, m. p. 96°.

2-*Pyrryl iodomethyl ketone*, C_6H_6ONI, forms faintly yellow needles, m. p. 81°. T. H. P.

Syntheses in the Pyrrole Group. IX. Pyrroylacetic Acid. BERNARDO ODDO and AUGUSTO MOSCHINI (*Gazzetta*, 1912, 42, ii, 267—269. Compare preceding abstract).—2-*Pyrroylacetic acid*,

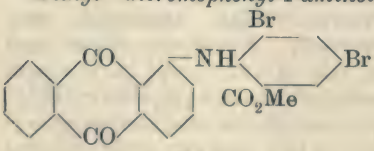
$$C_4NH_4\cdot CO\cdot CH_2\cdot CO_2H,$$

obtained as ester by the action of the chloride of monoethyl malonate on magnesium pyrryl bromide, forms slender, white needles, m. p. 95° (decomp.). The *ethyl* ester, $C_9H_{11}O_3N$, forms a felted mass of long, canary-yellow fibres, m. p. 71°, has the normal molecular weight in freezing benzene, and decomposes into $C_4NH_4\cdot COMe + CO_2 + Et\cdot OH$ when heated with dilute alkali; its alcoholic solution gives a green coloration with ferric chloride. T. H. P.

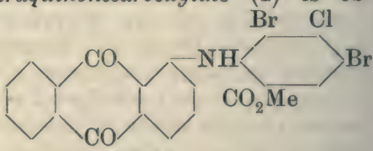
Preparation of Condensation Products in the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 246966. Compare Abstr., 1911, i, 855).—When the esters of arylaminoanthraquinonecarboxylic or diaryldiaminoanthraquinonedicarboxylic acids are reduced, they furnish acridone derivatives, which dye cotton.

1 : 5-*Anthraquinonediacridone*, a violet powder, is prepared by reducing dimethyl 1 : 5-dianilinoanthraquinone-*o*-dicarboxylate with zinc and 30% ammonium hydroxide.

Methyl dibromophenyl-1-*aminoanthraquinonecarboxylate* (I) is ob-

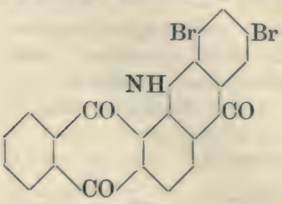


(I.)



(III.)

tained by condensing 1-chloroanthraquinone with methyl 3 : 5-dibromoanthranilate; on reduction with sodium hyposulphite it furnishes *dibromoanthracridone* (II), which is isolated in the form of red flakes by subsequent oxidation (aerial or otherwise).



(II.)

Methyl chlorodibromophenyl-1-*aminoanthraquinonecarboxylate* (III) is obtained in a similar manner from 1-chloroanthraquinone and methyl 4-chloro-3 : 5-dibromoanthranilate; on reduction it yields *chlorodibromoanthracridone*.

F. M. G. M.

Action of Heat on *d*-Lupanine, $C_{15}H_{24}ON_2$. S. Di Palma (*Chem. Zentr.*, 1912, i, 1839; from *Giorn. Pharm. Chim.*, 1912, 61, 152—166). —Lupanine melts to an orange liquid, which darkens, evolving vapours with an odour of pyridine. The residue contains a *base*, $C_{15}H_{22}N_2$, which forms a *platinichloride*, m. p. 117—119° after dehydration, an *aurichloride*, m. p. 160—165° (decomp.), and a *hydrochloride*, m. p. 165° (decomp.). C. H. D.

Hydantoins. XII. Synthesis of Thiotyrosine. Treat B. Johnson and Charles A. Brautlecht (*J. Biol. Chem.*, 1912, 12, 175—196. Compare this vol., i, 585).—2-*Thio*-1-*phenyl*-4-p-*nitrobenzylidenehydantoin*, $NO_2\cdot C_6H_4\cdot CH{:}C<\begin{matrix}CO\text{--}NPh\\ NH\cdot CS\end{matrix}$, prepared by condensation of nitrobenzaldehyde with thiophenylhydantoin, separates from glacial acetic acid in yellow prisms, m. p. 278—279°. When heated with ethyl bromide and sodium ethoxide in alcoholic solution, it yields 2-*ethylthiol*-1-*phenyl*-4-p-*nitrobenzylidenehydantoin*, yellow needles, m. p. 212—213°, which, when digested with hydrochloric acid, gives a quantitative yield of 1-*phenyl*-4-p-*nitrobenzylidenehydantoin*, needles, m. p. 300°. Reduction, by hydriodic acid and phosphorus, transforms this into 1-*phenyl*-4-p-*aminobenzylhydantoin*, prisms, m. p. 143°, the *hydriodide*, m. p. 275° (decomp.), *hydrochloride*, m. p. 260—262° (decomp.), *sulphate*, decomposing at 190—250° according to rate of heating, and *nitrate*, similarly decomposing at 190—240°, of which were also examined.

4-p-*Aminobenzylhydantoin hydrochloride* is obtained in good yield by the reduction of 4-*p*-nitrobenzylidenehydantoin by means of tin and hydrochloric acid, or by digestion of the corresponding *hydriodide* (formed in needles decomposing at 220° by reduction of *p*-nitrobenzylhydantoin with hydriodic acid and phosphorus) with an aqueous suspension of silver chloride. It forms prisms, m. p. 255—257° (decomp.), and, when treated with alkali, yields the corresponding 4-p-*aminobenzylhydantoin*, prisms, m. p. 145°. When diazotised and heated, the latter substance is transformed into tyrosinehydantoin, m. p. 258°.

4-p-*Nitrobenzylhydantoin*, pale yellow prisms, m. p. 238—240° (decomp.), obtained by nitration of benzylhydantoin at 0° by nitric acid (D 1·52), is transformed by tin and hydrochloric acid into the above-mentioned hydrochloride of 4-*p*-aminobenzylhydantoin.

When a solution of potassium xanthate is added to a diazotised solution of 4-aminobenzylhydantoin hydrochloride, 4-p-*diazobenzylhydantoin ethylxanthate* separates as an unstable voluminous, yellow precipitate, which, when allowed to remain at the ordinary temperature, or when heated at 90°, is converted into 4-*benzylhydantoin* p-*ethylxanthate*, $EtO\cdot SCS\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}CO\text{—}NH\\ NH\cdot CO\end{matrix}$, m. p. about 170° (decomp.). Saponification with alkali or digestion with water transforms this into *thiotyrosinehydantoin*, m. p. 248—249°, from which, after prolonged treatment with barium hydroxide, the *sulphate* of *thiotyrosine disulphide* is obtained. The latter, when heated with

water, deposits *thiotyrosine disulphide*, $[CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot C_6H_4]_2S_2$, m. p. 278° (decomp.), which can also be obtained directly by diazotising the hydrochloride of 4-*p*-aminobenzylhydantoin, addition of the requisite quantity of potassium xanthate, separation of the yellow diazonium compound, and treatment of the latter with boiling barium hydroxide solution. The disulphide is characterised by its very sparing solubility in organic media, except glacial acetic acid. It does not give Adamkiewicz's reaction, Millon's test, or the biuret reaction. When heated with concentrated sulphuric acid, it yields a purple colour, which disappears when the solution is diluted with water. This test serves to detect the presence of traces of thiotyrosine in tyrosine. Its *sulphate* and *hydrochloride*, decomposing at 278°, were analysed. The *dibenzoyl* derivative decomposes at about 200° (decomp.). Potassium cyanate transformed the hydrochloride of thiotyrosine disulphide into the corresponding *hydantoin*, $C_{20}H_{18}O_4N_4S_2$, which decomposes at about 278°. *Thiotyrosine hydrochloride*, m. p. 249° (decomp.), is obtained by reduction of the disulphide with tin and hydrochloric acid, and, when heated with ammonia, yields *thiotyrosine*,

$$HS \cdot C_6H_4 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H,$$

m. p. about 250°, according to mode of heating. The latter does not give Millon's test for tyrosine, and reacts with sulphuric acid in the same manner as the disulphide. A characteristic benzoyl derivative could not be prepared from it. It is very readily oxidised to the disulphide.

Thiotyrosine disulphide was also prepared from 1-phenyl-4-*p*-amino benzylhydantoin by diazotisation in hydrochloric acid solution, followed by addition of potassium xanthate, separation of the diazonium compound so formed, and treatment of the latter with water and barium hydroxide. Reduction of the disulphide thus prepared leads to the isolation of thiotyrosine hydrochloride. H. W.

Hydantoins. XIII. A New Method for the Synthesis of Phenylalanine. TREAT B. JOHNSON and WILLIAM B. O'BRIEN (*J. Biol. Chem.*, 1912, **12**, 205—213).—2-Thio-4-benzylidenehydantoin (Johnson and Nicolet, this vol., i, 53) when reduced by tin and hydrochloric acid gives an almost quantitative yield of phenylalanine.

2-Thio-4-benzylidenehydantoin, when treated with aqueous chloroacetic acid, is desulphurised, with the formation of 4-benzylidenehydantoin.

When phenylalanine and potassium thiocyanate are heated during thirty minutes in a mixture of acetic acid and acetic anhydride, a quantitative yield of 2-*thio*-3-*acetyl*-4-*benzylhydantoin*, m. p. 257°, is obtained; this, when hydrolysed by hydrochloric acid, yields 2-*thio*-4-*benzylhydantoin*, m. p. 185°. Desulphurisation by means of aqueous chloroacetic acid converts this compound into the hydantoin of phenylalanine, m. p. 190°.

2-*Thio*-3-*benzoylhydantoin* was condensed with anisaldehyde in the presence of sodium acetate and acetic acid to 2-*thio*-4-*anisylidenehydantoin*, m. p. 257° (decomp.), and with piperonal to 2-*thio*-4-*piperonylidenehydantoin*, decomposing above 285°. H. W.

Hydantoins. XIV. The Action of Potassium Thiocyanate on Asparagine. TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1912, **48**, 103—111. Compare preceding abstracts).—Aspartic acid like glutamic acid (Johnson and Guest, this vol., i, 316) when treated with potassium thiocyanate in acetic anhydride solution yields practically no thiohydantoin derivative, the amido-nitrogen of the acid being eliminated as ammonia.

Asparagine, on the other hand, reacts normally with the above reagents, producing *2-thio-3-acetylhydantoin-4-acetamide*,

$$NH_2\cdot CO\cdot CH_2\cdot CH{<}\begin{matrix}CO-NH\\ | \\ NAc\cdot CS\end{matrix},$$

prismatic crystals, m. p. 222—223° (decomp.); a small amount of *2-thiohydantoin-4-acetamide*, m. p. 246° (decomp.), is obtained at the same time. By hydrolysis of the first compound there is formed *2-thiohydantoin-4-acetic acid*, hexagonal plates, m. p. 222° (decomp.); this substance can be desulphurised by digesting with an aqueous solution of chloroacetic acid, when the product is hydantoin-4-acetic acid, $CO_2H\cdot CH_2\cdot CH{<}\begin{matrix}CO-NH\\ | \\ NH\cdot CO\end{matrix}$, m. p. 214—215° (compare Dakin, Abstr., 1910, i, 590; Lippich, Abstr., 1908, 861; etc.). D. F. T.

Hydantoins. XV. The Desulphurisation of 2-Thiohydantoins. TREAT B. JOHNSON, GEORGE MORTON PFAU, and WILLARD WELLINGTON HODGE (*J. Amer. Chem. Soc.*, 1912, **34**, 1041—1048).—A further continuation of the investigation on the desulphurisation of 2-thiodantoins by chloroacetic acid (compare preceding abstract; also Wheeler and Liddle, Abstr., 1908, i, 692; and Johnson and Nicolet, this vol., i, 52); it is found that the action of chloroacetic acid on disubstituted thiocarbamides is of a different nature, producing thiazole derivatives.

2-Thio-1-*p*-tolylhydantoin, $C_6H_4Me\cdot N{<}\begin{matrix}CO\cdot CH_2\\ | \\ CS\cdot NH\end{matrix}$, is obtained by warming a solution of *p*-tolyl thiocarbimide with glycine and an equimolecular quantity of potassium hydroxide; it forms yellow crystals, m. p. 228° (compare Marckwald, Neumark, and Stelzner, Abstr., 1892, 149), and on heating with an aqueous solution of chloroacetic acid is converted into 1-p-*tolylhydantoin*, m. p. 206°; the action of benzaldehyde on this substance in the presence of sodium acetate and acetic acid gives 1-p-*tolyl-4-benzylidenehydantoin*, $C_6H_4Me\cdot N{<}\begin{matrix}CO\cdot C:CHPh\\ | \\ CO\cdot NH\end{matrix}$, plates, m. p. 259°, which can also be obtained by the action of chloroacetic acid on 2-*thio*-1-p-*tolyl-4-benzylidenehydantoin*, plates, m. p. 188°, obtained in an analogous manner from the thio-*p*-tolylhydantoin.

2-*Thio*-1-*benzylhydantoin*, obtained from benzyl thiocarbimide and glycine, has m. p. 128°.

When *s*-phenyl-*p*-tolylthiocarbamide, *p*-tolylthiocarbamide, or *s*-*p*-tolylpiperidylthiocarbamide are digested with chloroacetic acid solution, the product in each case is 2:4-diketo-3-*p*-tolyltetrahydrothiazole, $C_6H_4Me\cdot N{<}\begin{matrix}CO\cdot CH_2\\ | \\ CO\cdot S\end{matrix}$.

For the smooth interaction of *o*-tolylthiocarbimide and glycine to

form 2-thio-1-*o*-tolylhydantoin, yellow plates, m. p. 149—150° (compare Marchwald, Neumark, and Stelzner, *loc. cit.*), the presence of two molecular proportions of potassium hydroxide is necessary; the product can be desulphurised by chloroacetic acid to 1-*o*-*tolylhydantoin*, prismatic crystals, m. p. 148°; this is almost quantitatively converted by benzaldehyde into 1-*o*-*tolyl*-4-*benzylidenehydantoin*, prismatic crystals, m. p. 193—194°, which is also obtained when 2-*thio*-1-*o*-*tolyl*-4-*benzylidenehydantoin* (prisms, 165°), the product of the action of thio-*o*-tolylhydantoin and benzaldehyde, is desulphurised.

Contrary to a previous statement (Brautlecht, Abstr., 1911, i, 922), 2-thio-1-phenylhydantoin is easily converted by digestion with a concentrated aqueous solution of chloroacetic acid into 1-phenylhydantoin. D. F. T.

Hydantoins. XVI. The Alkylation of 2-Thio-4-benzylidenehydantoin. Treat B. Johnson and Ben H. Nicolet (*J. Amer. Chem. Soc.*, 1912, **34**, 1048—1054. Compare Johnson and Nicolet, this vol., i, 585).—The alkylation of the aldehyde condensation products of hydantoin and 2-thiohydantoin is of especial interest on account of the similarity in the structure of these substances and of uracil and thiouracil.

Methylation of 2-thio-4-benzylidenehydantoin (Wheeler, Nicolet, and Johnson, Abstr., 1911, i, 1031), with excess of methyl iodide in the presence of one molecular proportion of potassium hydroxide yields 2-*methylthiol*-4-*benzylidene*-1 : 5-*dihydro*-5-*glyoxalone*,

$$CHPh:C<\begin{matrix}CO\cdot NH \\ N{=}C\cdot SMe\end{matrix},$$

creamy needles, m. p. 202°, which can be hydrolysed by concentrated hydrochloric acid to 4-benzylidenehydantoin. Methylation of the original substance with two molecular proportions of sodium ethoxide and excess of methyl iodide produces 2-*methylthiol*-4-*benzylidene*-1-*methyl*-1 : 5-*dihydro*-5-*glyoxalone*, yellow prisms, m. p. 105°, which on hydrolysis gives 4-*benzylidene*-1-*methylhydantoin*, flat, colourless prisms, m. p. 221°.

Alkylation of 2-thio-4-benzylidenehydantoin with ethyl iodide gives 2-*ethylthiol*-4-*benzylidene*-1 : 5-*dihydro*-5-*glyoxalone*, pale yellow needles, m. p. 165—166°, which can be methylated to 2-*ethylthiol*-4-*benzylidene*-1-*methyl*-1 : 5-*dihydro*-5-*glyoxalone*, yellow, prismatic crystals, m. p. 94—95°. If the original alkylation with ethyl iodide be performed in the presence of sodium ethoxide, the product is 2-*ethylthiol*-4-*benzylidene*-1-*ethyl*-1 : 5-*dihydro*-5-*glyoxalone*, an oil which on hydrolysis yields 4-*benzylidene*-1-*ethylhydantoin*, colourless prisms, m. p. 160°; this can also be obtained by the action of ethyl bromide and alkali on 4-benzylidenehydantoin, and by further treatment with methyl iodide and sodium ethoxide is converted into 4-*benzylidene*-3-*methyl*-1-*ethylhydantoin*, yellow flakes, m. p. 94°; also by alkylation with ethyl bromide it gives 4-*benzylidene*-1 : 3-*diethylhydantoin*, m. p. 91—92°.
D. F. T.

Hydantoins. XVII. Synthesis of the Hydantoin of 3-Aminotyrosine. Treat B. Johnson and Robert Bengis (*J. Amer. Chem. Soc.*, 1912, **34**, 1054—1061).—4-*Anisylhydantoin*,

$OMe\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix} CO-NH \\ NH-CO \end{matrix}$, m. p. 175—176°, together with a certain amount of *anisylhydantoic acid*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot NH_2,$$

m. p. 156°, is obtained by the reduction of 4-anisylidenehydantoin (Wheeler and Hoffman, Abstr., 1911, i, 498) in aqueous suspension with sodium amalgam; on treatment with a mixture of concentrated and fuming nitric acid, it yields 4-m-*nitro*-p-*methoxybenzylhydantoin*, prisms, m. p. 186—188°, with half a molecule of water of crystallisation (compare Johnson and Brautlecht, Abstr., 1911, i, 813); this can be quantitatively reduced by ferrous sulphate and ammonia solution to 4-m-*amino*-p-*methoxybenzylhydantoin*, a crystalline solid, m. p. 175—177°, *hydrochloride*, needles, m. p. 271—272° (decomp.); the constitution of this base is proved by its identity with that of the base mentioned below.

m-Nitro-*p*-methoxybenzaldehyde, m. p. 83°, obtained by nitration of anisaldehyde, condenses with hydantoin when heated with sodium acetate and acetic acid, producing 4-m-*nitro*-p-*methoxybenzylidenehydantoin*, flat prisms (from acetic acid), containing one molecule of acetic acid of crystallisation, m. p. 276—277° (decomp.); this is reduced by phosphorus and hydriodic acid to 4-m-*amino*-p-*hydroxybenzylhydantoin* (the hydantoin of aminotyrosine), *hydrochloride*, prismatic crystals, m. p. 254° (decomp.), containing one molecule of water of crystallisation; reduction by ferrous sulphate and ammonia, on the other hand, affects only the nitro-group, producing 4-m-*amino*-p-*methoxybenzylidenehydantoin*, *hydrochloride*, needles, m. p. 285—286° (decomp.); this base can be further reduced by tin and hydrochloric acid to the above 4-*m*-amino-*p*-methoxybenzylhydantoin, hydrochloride, m. p. 271—272°.

The action of ordinary concentrated nitric acid on 4-anisylidenehydantoin causes oxidation to a glycol derivative, 4-*hydroxy*-4-α-*hydroxy* m-*nitro*-p-*methoxybenzylhydantoin*,

$$OMe\cdot C_6H_3(NO_2)\cdot CH(OH)\cdot C(OH)<\begin{matrix} CO-NH \\ NH\cdot CO \end{matrix},$$

yellow needles, m. p. 206—207°. D. F. T.

Hydantoins. XVIII. Synthesis of 3-Bromotyrosine. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1912, **34**, 1061—1066).—*m*-Bromoanisaldehyde (pale yellow prisms, m. p. 52—53°, from the action of bromine on anisaldehyde) condenses with hydantoin under the usual treatment, producing 4-m-*bromo*-p-*methoxybenzylidenehydantoin*, yellow needles, m. p. 267—268°, which can be reduced in alcoholic solution by tin and hydrogen chloride to 4-m-*bromo*-p-*methoxybenzylhydantoin*, triclinic crystals, m. p. 210—211°. This last substance can also be obtained from 4-*m*-amino-*p*-methoxybenzylhydantoin (Johnson and Bengis, preceding abstract) by diazotisation and subsequent treatment with a solution of cuprous bromide. On heating with barium hydroxide solution under pressure, the hydantoin ring is disrupted with formation of α-*amino*-β-m-*bromo*-p-*methoxyphenylpropionic acid* $OMe\cdot C_6H_3Br\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, rect-

angular plates, m. p. 235—236° (decomp.); this acid is easily demethylated by boiling with hydrobromic acid, with the production of 3-*bromotyrosine*, $OH\cdot C_6H_3Br\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,H_2O$, tetrahedral crystals of sweet taste, m. p. 247—248° (decomp.), *hydrobromide*, m. p. 190—191° (decomp.); *picrate* and *platinichloride* are extremely soluble in water.

m-Bromo-*p*-hydroxybenzaldehyde condenses with hydantoin, giving a poor yield of 4-m-*bromo*-p-*hydroxybenzylidenehydantoin*, yellow needles, decomposing at 295°; this is reduced by hydriodic acid to 4-*p*-hydroxybenzylhydantoin (tyrosinehydantoin).

4-*m*-Amino-*p*-hydroxybenzylhydantoin (Johnson and Bengis, *loc. cit.*), when diazotised and treated with cuprous bromide solution, gives 4-m-*bromo*-p-*hydroxybenzylhydantoin* (3-*bromotyrosinehydantoin*), $OH\cdot C_6H_3Br\cdot CH_2\cdot CH<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, prisms, m. p. 284—285° (decomp.).

D. F. T.

Hydantoins. XIX. Synthesis of 5-Thiohydantoins. TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1912, **34**, 1208—1213).—Although carbethoxyglycinamide does not undergo condensation to hydantoin (Fischer and Otto, Abstr., 1893, i, 608), it is found that the thioamide condenses smoothly, whereas in the cases of the isomeric ethyl hydantoates it is the thio-ester which is indifferent (compare Harries and Weiss, Abstr., 1893, i, 738). The phenylated thioamides are also found to condense, resembling the substituted carbethoxyglycinamides of Lehmann (Abstr., 1901, i, 275) and of Clark and Francis (Trans., 1911, **99**, 319).

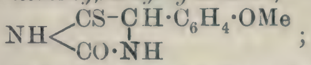
5-*Thiohydantoin*, $NH<\begin{matrix}CS-CH_2\\ CO\cdot NH\end{matrix}$, obtained by dissolving carbethoxyaminoacet-thioamide (this vol., p. 305) in 5—10% sodium hydroxide containing one molecular proportion of alkali and acidifying, crystallises from hot water in colourless, lanceolate crystals, which decompose above 220°. Unlike 2-thiohydantoin, it undergoes oxidation in aqueous or alkaline solution, the latter changing colour from pink to deep red. Concentrated hydrochloric acid converts it into hydrogen sulphide and hydantoin, and it yields with benzaldehyde a brownish-yellow, insoluble product. *Anilinophenylacetothioamide*,

$$C_6H_5\cdot CH(NHPh)\cdot CS\cdot NH_2,$$

prepared by the addition of hydrogen sulphide to anilinophenylacetonitrile (Knoevenagel, Abstr., 1904, i, 989), crystallises from spirit in long, slender prisms, m. p. 130°; similarly, *carbethoxyaminophenylacetothioamide*, $C_6H_5\cdot CH(NH\cdot CO_2Et)\cdot CS\cdot NH_2$, from urethanophenylacetonitrile (Lehmann, *loc. cit.*), crystallises in colourless needles, m. p. 127°, which dissolve in 10% sodium hydroxide, yielding the stable 5-*thio*-4-*phenylhydantoin*, $NH<\begin{matrix}CS-CHPh\\ CO\cdot NH\end{matrix}$, as a yellow powder, decomposing at about 259°. Condensation of urethane with *p*-methoxymandelonitrile in presence of zinc chloride furnishes *carbethoxyamino*-p-*methoxyphenylacetonitrile*,

$$OMe\cdot C_6H_4\cdot CH(NH\cdot CO_2Et)\cdot CN,$$

m. p. 117°, which may be converted into the *thioamide*, m. p. 146°, and this into 5-*thio*-4-p-*methoxyphenylhydantoin*,



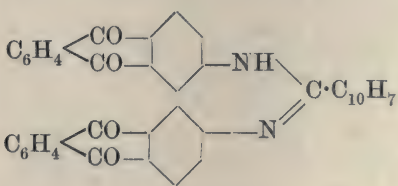
this separates as a yellow solid decomposing at about 263°.

J. C. W.

1 : 5-Naphthylenediamine. FRANZ KUNCKELL and HANNS SCHNEIDER (*Chem. Zeit.*, 1912, 36, 1021).—1 : 5-Naphthylenediamine, dissolved in benzene, was treated with acetic anhydride, whereby the corresponding *diacetyl* compound, m. p. about 360°, was obtained in poor yield. The authors have made the unpleasant discovery that this compound causes violent irritation of the skin. Since 1 : 5-naphthylenediamine has been investigated by a number of chemists and no such unpleasant action has been noted, it would appear that the latter is a specific property of the acetyl derivative.

H. W.

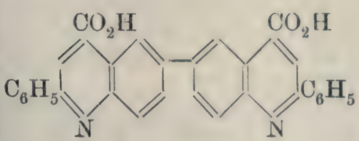
Preparation of Condensation Products in the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 246477).—The *compound* (annexed formula) is obtained when a fusion of 2-aminoanthraquinone (10 parts), naphthalene (50 parts), and copper (0·5 part) is carefully treated at 100—120° with carbon tetrachloride, the temperature raised to 140—150°, and maintained until evolution of hydrogen chloride ceases; it crystallises from chlorobenzene, and has m. p. 298—302° (about).



The analogous *compound* obtained by replacing the naphthalene with diphenyl dissolves in acetic acid; these products furnish on sulphonation readily soluble *sulphonic acids*, which dye wool in yellow shades.

F. M. G. M.

Preparation of 2-Phenyl- and Substituted 2-Phenyl-6 : 6′-diquinolyl-4 : 4′-dicarboxylic Acids, their Homologues and Derivatives. CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.-P. 246078).—2-Phenylquinoline-4-carboxylic acid, prepared from aniline, benzaldehyde, and pyruvic acid, has previously been described; it is now found that analogous reactions take place when the aniline is replaced by benzidine, tolidine, or dianisidine, and the benzaldehyde by substituted benzaldehydes, yielding substituted phenyldiquinolylcarboxylic acids.



6 : 6′-*Diquinolyl*-2 : 2′-*diphenyl*-4 : 4′-*dicarboxylic acid* (annexed formula), m. p. 225°, is prepared by boiling together an alcoholic solution of benzidine (65 parts), pyruvic acid (61 parts), and benzaldehyde (75

parts) during several hours, when the product separates in yellowish-brown crystals.

6 : 6′-*Diquinolyl*-2 : 2′-*dihydroxydiphenyl*-4 : 4′-*dicarboxylic acid*, m. p. 248°, is obtained when the benzaldehyde in the foregoing reaction is replaced by salicylaldehyde, whilst 6 : 6′-*diquinolyl*-2 : 2′-*diphenyl*-8 : 8′-*dimethyl*-4 : 4′-*dicarboxylic acid*, a yellow powder, results from the employment of *o*-toluidine; it is insoluble in the ordinary organic solvents and does not melt below 300°.

8 : 8′-*Dimethoxy*-6 : 6′-*diquinolyl*-2 : 2′-*diphenyl*-4 : 4′-*dicarboxylic acid*, m. p. 290° (about), is prepared in an analogous manner from *o*-dianisidine. F. M. G. M.

Compounds of Certain Hydrated Metallic Salts with Caffeine. FILIPPO CALZOLARI (*Gazzetta*, 1912, **42**, ii, 15—21).—The addition of caffeine to concentrated solutions of salts yields the following compounds, which are stable to the action of air and light, and are decomposed by water, alcohol or chloroform in the cold with separation of caffeine: $MgI_2,8H_2O,2C_8H_{10}O_2N_4$; $MnI_2,8H_2O,2C_8H_{10}O_2N_4$; $CoI_2,8H_2O,2C_8H_{10}O_2N_4$; $NiI_2,8H_2O,2C_8H_{10}O_2N_4$;

$Mg(ClO_4)_2,8H_2O,2C_8H_{10}O_2N_4$;

$Mn(ClO_4)_2,8H_2O,2C_8H_{10}O_2N_4$; $Co(ClO_4)_2,8H_2O,2C_8H_{10}O_2N_4$;

$Ni(ClO_4)_2,8H_2O,2C_8H_{10}O_2N_4$;

$Mg(SCN)_2,6H_2O,2C_8H_{10}O_2N_4$; $Mn(SCN)_2,8H_2O,2C_8H_{10}O_2N_4$;

$Fe(SCN)_2,8H_2O,2C_8H_{10}O_2N_4$;

$Co(SCN)_2,8H_2O,2C_8H_{10}O_2N_4$; $Ni(SCN)_2,8H_2O,2C_8H_{10}O_2N_4$;

$Ni(NO_3)_2,8H_2O,2C_8H_{10}O_2N_4$,

(compare Barbieri and Calzolari, Abstr., 1911, i, 184, 266, 268; Barbieri and Lanzoni, Abstr., 1911, i, 268). T. H. P.

Etherification of *o*-Hydroxyazo-compounds. I. G. CHARRIER and G. FERRERI (*Atti R. Accad. Sci. Torino*, 1912, **47**, 811—840; *Gazzetta*, 1912, **42**, ii, 117—144).—It has been previously shown (Abstr., 1910, i, 287; 1911, i, 1045) that *o*-aminoazo- and *o*-hydroxyazo-compounds tend to react as true azo-compounds, for instance, $NH_2\cdot C_{10}H_6\cdot N{:}NPh$ and $OH\cdot C_{10}H_6\cdot N{:}NPh$, and not as the tautomeric forms, $NH{:}C_{10}H_6{:}N\cdot NHPh$ and $O{:}C_{10}H_6{:}N\cdot NHPh$, containing a quinonoid instead of an aromatic nucleus. Also, in their reactions with alkyl sulphates, the *o*-hydroxyazo-compounds are now found to behave as true azo-compounds, and a series of methyl and ethyl ethers of the general formula $OR\cdot C_{10}H_6\cdot N{:}NAr$ have been prepared. These ethers are decomposed by nascent hydrogen according to the equation: $OR\cdot C_{10}H_6\cdot N_2\cdot Ar + 2H_2 = NH_2Ar + OR\cdot C_{10}H_6\cdot NH_2$, whilst with nitric acid they give ethers of dinitronaphthols and diazonium nitrates:

$$OR\cdot C_{10}H_6\cdot N_2\cdot Ar + 3HNO_3 = OR\cdot C_{10}H_5(NO_2)_2 + NO_3\cdot NAr{\vdots}N.$$

The ethers crystallise well and are readily hydrolysed by dilute mineral acids, but show great stability towards alkalis. They exhibit marked basic properties, forming salts with mineral acids and unstable double salts with mercuric, platinic, and stannic chlorides, etc.

1-*Benzeneazo-2-naphthyl methyl ether*, $OMe\cdot C_{10}H_6\cdot N{:}NPh$, prepared by the interaction of 1-benzeneazo-2-naphthol and methyl sulphate in sodium hydroxide solution (30%), forms garnet-red plates m. p. 62°, and

dissolves in dilute mineral acids, giving intense red colorations, and in concentrated sulphuric acid, forming a ruby-red solution; its *hydrochloride*, $C_{17}H_{14}ON_2,HCl$, forms red crystals with metallic lustre. 1-*Amino-2-naphthyl methyl ether*, $NH_2\cdot C_{10}H_6\cdot OMe$, obtained together with aniline by the action of nascent hydrogen on the methoxyazo-compound, forms silky, white needles, m. p. 53°. 1-*Acetylamino*-2-*naphthyl methyl ether* forms white prisms, m. p. 178°. 1:6-*Dinitro*-2-*naphthyl methyl ether*, $OMe\cdot C_{10}H_5(NO_2)_2$, crystallises in pale yellow needles, m. p. 157—158°.

1-o-*Tolueneazo-2-naphthyl methyl ether*, $OMe\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4Me$, forms red leaflets, m. p. 58°, and gives a ruby-red solution in concentrated sulphuric acid and red solutions in dilute mineral acids. The *hydrochloride*, $C_{18}H_{16}ON_2,HCl$, forms cantharides-green needles.

1-p-*Tolueneazo-2-naphthyl methyl ether* crystallises in garnet-red plates, m. p. 68°, and yields red solutions in concentrated sulphuric and dilute mineral acids. The *hydrochloride* forms minute, green needles with metallic lustre.

1-o-*Methoxybenzeneazo-2-naphthyl methyl ether*,

$$OMe\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot OMe,$$

prepared from either 1-*o*-hydroxybenzeneazo-2-naphthol or 1-*o*-anisylazo-2-naphthol by the action of methyl sulphate and sodium hydroxide, forms mammillary masses of bright red leaflets with a golden lustre, m. p. 93—94°, and gives a red solution in concentrated sulphuric acid. The *hydrochloride*, $C_{18}H_{16}O_2N_2,HCl$, separates in emerald-green needles.

1-p-*Hydroxybenzeneazo-2-naphthol*, $OH\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot OH$, prepared by the action of *p*-hydroxybenzenediazonium chloride on β-naphthol in alkaline solution, forms cantharides-green needles or leaflets, m. p. 194°. 1-p-*Acetoxybenzeneazo-2-naphthol*,

$$OH\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot OAc,$$

crystallises in shining orange-red needles, m. p. 115°, and the corresponding *benzoyl* derivative, $C_{23}H_{16}O_3N_2$, in red needles, m. p. 164°.

1-p-*Methoxybenzeneazo-2-naphthyl methyl ether*,

$$OMe\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot OMe,$$

obtained by the interaction of methyl sulphate and 1-*p*-hydroxybenzeneazo-2-naphthol in 30% sodium hydroxide solution, forms prismatic needles, m. p. 107°, and dissolves in sulphuric acid with red coloration. Its *hydrochloride*, $C_{18}H_{16}O_2N_2,HCl$, separates in emerald-green needles showing metallic lustre.

The action of methyl sulphate on 1-*p*-hydroxybenzeneazo-2-naphthol in 15% sodium hydroxide solution yields: (1) 1-p-*methoxybenzeneazo*-2-*naphthol*, $OH\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot OMe$, m. p. 137°, and (2) 1-p-*hydroxybenzeneazo-2-naphthyl methyl ether*, $OMe\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot OH$, which crystallises in reddish-brown leaflets, m. p. 225° (decomp.), and dissolves in sulphuric acid with a red coloration, and in dilute solutions of alkali hydroxides or carbonates, or ammonia, giving yellow or orange liquids according to the concentration; its *hydrochloride*,

$$C_{17}H_{14}O_2N_2,HCl,$$

forms emerald-green needles with metallic lustre.

1-o-*Methoxybenzeneazo-2-naphthyl ethyl ether*,

$$OEt\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot OMe,$$

forms bright red leaflets, m. p. 75°, its *hydrochloride*, $C_{19}H_{18}O_2N_2,HCl$, giving red crystals.

1-p-*Methoxybenzeneazo-2-naphthyl ethyl ether* crystallises in red, prismatic plates, m. p. 52—53°, and its *hydrochloride* in greenish-brown needles.

1-o-*Ethoxybenzeneazo-2-naphthyl methyl ether*,

$$OMe\cdot C_{10}H_6\cdot N:N\cdot C_6H_4\cdot OEt,$$

forms long, flat, red needles or golden-yellow plates, m. p. 136°; its *hydrochloride* separates in metallic, green needles.

1-o-*Ethoxybenzeneazo-2-naphthyl ethyl ether*,

$$OEt\cdot C_{10}H_6\cdot N:N\cdot C_6H_4\cdot OEt,$$

crystallises in pale red needles, m. p. 102°, and its *hydrochloride* as a reddish-brown powder with a green, metallic lustre.

1-p-*Ethoxybenzeneazo-2-naphthyl methyl ether*,

$$OMe\cdot C_{10}H_6\cdot N:N\cdot C_6H_4\cdot OEt,$$

forms flat, orange needles, m. p. 113°, and its *hydrochloride*, green crystals with a golden, metallic lustre.

1-p-*Ethoxybenzeneazo-2-naphthyl ethyl ether* forms orange-yellow needles, m. p. 81°.

1-a-*Naphthaleneazo-2-naphthyl methyl ether*, $OMe\cdot C_{10}H_6\cdot N:N\cdot C_{10}H_7$, separates in reddish-brown leaflets, m. p. 67°, and its *hydrochloride* in cantharides-green crystals.

1-a-*Naphthaleneazo-2-naphthyl ethyl ether* forms flat, dark garnet-red needles, m. p. 105—106°, and its *hydrochloride*, a green, crystalline mass with a metallic lustre.

1-β-*Naphthaleneazo-2-naphthyl methyl ether* crystallises in garnet-red prisms, m. p. 94—95°, and its *hydrochloride* in slender, metallic green needles. T. H. P.

Preparation of Chloro-1-diazo-2-oxy- and of Chloro-2-diazo-1-oxy-naphthalenesulphonic Acids. KALLE & Co. (D.R.-P. 246573 and 246574).—The chlorination of *o*-diazo-oxynaphthalene-sulphonic acids has not previously proved satisfactory; it is now found to proceed smoothly at higher temperatures and in the presence of sulphuric acid containing sulphur trioxide.

1-Diazo-2-oxynaphthalene-4-sulphonic acid (125 parts), dissolved in concentrated sulphuric acid (285 parts), is treated at a temperature not exceeding 20° with 100 parts of sulphuric acid containing 70% anhydride, and subsequently maintained at 50° during the passage of a stream of chlorine; the *chloro-1-diazo-2-oxy-4-naphthalenesulphonic acid* is isolated as a yellow, crystalline powder.

The chlorination of 2-diazo-1-oxynaphthalene-5-sulphonic acid is carried out in a similar manner, but at lower temperatures (10—15° and 40—45° respectively).

The second patent states that a more satisfactory method consists in lowering the temperature in both cases to about 10°, but forcing an excess of chlorine in under a pressure of 7—8 atmospheres in the first case and 5—6 atmospheres in the second, and keeping the mixtures continually agitated during about twelve hours at the ordinary temperature. *Chloro-2-diazo-1-oxynaphthalene-5-sulphonic acid* forms pale greenish-grey crystals. F. M. G. M.

Amylases. IV. A Further Investigation of the Properties of Pancreatic Amylase. HENRY CLAPP SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1912, **34**, 1104—1111. Compare Abstr., 1911, i, 827).—Preparations of pancreatic amylase made during the summer months proved to be less active than those obtained during colder weather; a method of preparation is now described with special precautions as to temperature.

Recalculation of the composition of the amylase on the assumption that the apparent ash is mainly phosphoric acid gives a composition C 51·9, H 6·6, N 15·3, S 1·0, P 0·8, O (and undetermined) 24·4, which is rather similar to that of casein; the heat of combustion (5568 calories per gram) is, however, rather lower than that of casein (5629). The aqueous solution of the amylase (which coagulates completely at 70°) shows great activity towards starch, and a portion of one preparation hydrolysed 1,000,000 times its weight of starch (the concentration of the amylase in this solution was 1 : 100,000,000) to the erythrodextrin stage in thirty hours, and to products exhibiting no reaction with iodine in forty-eight to ninety-six hours. The sugars formed were maltose and dextrose. The enzyme, which also shows proteoclastic power, deteriorates rapidly when dissolved in pure water, but retains its activity for a much longer period in aqueous solution containing sodium chloride and sodium phosphate, or when dissolved in 50% alcohol or acetone. D. F. T.

The Proteolytic Action of Taka-diastase. OLGA SZÁNTÓ (*Biochem. Zeitsch.*, 1912, **43**, 31—43).—Acids inhibit the action of taka-diastase in very low concentration. The inorganic acids inhibit Taka-diastase much less than they do trypsin. On the other hand, Taka-diastase is far more sensitive towards organic acids. In addition to the inhibiting action, acids also destroy the ferment. Hydrochloric acid acts the most strongly; its destructive power on trypsin is much less than that on Taka-diastase. In spite of their strong inhibitory action, organic acids only have a weak destructive action on the ferment. Alkalis also inhibit the action, but much less than acids. They do not possess a destructive power. Salts, with the exception of sodium lactate, have but little effect on the proteolytic action of Taka-diastase. The inhibitory action of sodium lactate on this ferment is about three times as great as it is on trypsin. Dextrose, lactose, and starch have no action, whereas lævulose has a slight inhibitory action. S. B. S.

The Relation of Certain Nucleic Acids to Enzymes which Split Glucosides. HELENE TSCHERNORUTZKY (*Zeitsch. physiol. Chem.* 1912, **80**, 298—306).—The glucoside structure of nucleic acids (Steudel) led to the enquiry whether emulsin and myrosin will split nucleic acids. The answer is in the affirmative, but consideration of the quantitative yield of purine substances and phosphoric acid liberated, finally led to the conclusion that the cleavage in question was due, not to the enzymes mentioned, but to nucleases mixed with them. W. D. H.

Enzyme Action. XVI. Enzymes of the Emulsin Type. I, Prunase, the Correlate of Prunasin. HENRY E. ARMSTRONG, EDWARD F. ARMSTRONG, and EDWARD HORTON (*Proc. Roy. Soc.*, 1912, *B*, 85, 359—362. Compare this vol., i, 594).—The conclusion was previously drawn that the action of almond emulsin on amygdalin is effected through the agency of two distinct enzymes: amygdalase, by which the amygdalin is converted into dextrose and Fischer's glucoside (*d*-mandelonitrile), and β-glucase, by which the latter glucoside is further resolved into dextrose and phenylhydroxyacetonitrile. This conclusion is verified by the discovery in the leaf of the cherry laurel (*Prunus laurocerasus*) of a β-glucase which is without action on amygdalin, yet readily decomposes Fischer's glucoside.

The name *prunasin* is given to Fischer's glucoside, on account of its general occurrence in the various species of *Prunus*, and the enzyme is termed *prunase*.

Prunasin is found to occur in the leaf of these plants, whereas amygdalin has only been found in the fruit kernel; the two enzymes are found to occur in a corresponding manner.

A discussion on the selective action of enzymes is given. W. J. Y.

Enzyme Action. XVII. Enzymes of the Emulsin Type. II. The Distribution of β-Enzymes in Plants. HENRY E. ARMSTRONG, EDWARD F. ARMSTRONG, and EDWARD HORTON (*Proc. Roy. Soc.*, 1912, *B*, 85, 363—369. Compare preceding abstract).—Several plants were tested with regard to their hydrolytic activity towards the glucosides linamarin, amygdalin, prunasin, and salicin in order to determine the distribution of the enzymes linase, amygdalase, prunase, and salicase.

The material was washed, cut up in a mincing machine, dried, and ground to a fine powder, and employed as such in the experiments. The extent of hydrolysis of the first three glucosides was determined by the quantity of hydrogen cyanide set free, and of the salicin by the dextrose liberated. The results, given in a table, show that amygdalase is sparsely distributed, and is almost confined to those seeds of plants in which amygdalin is present. Prunase is widely distributed, and the experiments point to the probability that a distinct enzyme, salicase, does exist, which is only capable of acting on salicin. On the other hand, prunase appears to act on salicin but less actively than on prunasin. It is possible that prunase, which is controlled by dextrose, becomes attached to the dextrose section of the molecule, and for this reason is able to attack so large a proportion of the β-glucosides.

In most cases, it is noticed that the quantity of hydrogen cyanide obtained varies with the season at which the plants were gathered.

The enzymes occurring together with many of the glucosides may owe their specific character to the fact that they act, not through the dextrose group of the molecule, but with the radicle associated with it, and with which they are compatible. W. J. Y.

Enzyme Action. XVIII. Enzymes of the Emulsin Type. III. Linase and Other Enzymes in Linaceæ. HENRY E. ARMSTRONG and J. VARGAS EYRE (*Proc. Roy. Soc.*, 1912, *B*, 85, 370—378. Compare preceding abstract).—The name *linase* is given

to the enzyme occurring in a large number of species of *Linaceae*, which hydrolyses the glucoside linamarin (phaseolunatin). A study of the enzymes present in the leaf and seed of sixty species of the *Linaceae* has been made with the same glucosides and in a similar manner to that given in the preceeding abstract. The enzymic activity towards these glucosides is correlated with the presence of a cyanophoric glucoside; thus the yellow-flowered species, which are free from cyanophoric glucosides, exhibit little activity towards the four glucosides employed, whereas the blue-, white-, or red-flowered varieties all yield hydrogen cyanide. The amount of both enzymes and glucosides in the plants vary with the period of growth. In all but one case the prunasin was hydrolysed to a very much less extent than the linamarin. The activity towards linamarin is attributed to the enzyme linase alone, and as this enzyme is accompanied by prunase in the *linaceae* and also in *Phaseolus lunatus*, it is possible that the former enzyme is without action on prunasin.

From the values obtained with salicin it is questionable whether linase has any action on this substance. W. J. Y.

Exciting Action of Alkalis, Especially Ammonia, on Peroxydases. JULES WOLFF (*Compt. rend.*, 1912, **155**, 484—486. Compare Abstr., 1909, i, 862).—Barley sprouts, 0·1 metre high, contain an active peroxydase unassociated with catalase, tyrosinase, or laccase. This peroxydase is rendered much less active on addition of ammonia, but in contact with this reagent, it regains its activity and at the end of fourteen hours attains a maximum activity twice as great as the original, which it retains for some hours and then gradually loses. An analogous series of changes takes place in the presence of sodium hydroxide, but much more rapidly, this reagent destroying the enzyme more quickly than ammonia. Sulphuric and phosphoric acids, even when very dilute, reduce the activity. The foregoing results were obtained with guaiacol as a test of oxidising capacity. With pyrogallol or quinol, on the contrary, ammonia appears to increase the activity of the enzyme immediately, and there is no variation in activity on keeping. T. A. H.

The Influence of Toluene on Zymases and Phosphatese. HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1912, **80**, 175—181).—Living yeast which under normal conditions in solutions containing phosphates produces no ester formation, produces in the presence of toluene a rapid formation of large amounts of a phosphate-carbohydrate combination. W. D. H.

A New Glucolytic Ferment of Yeast. VICTOR BIRCKNER (*J. Amer. Chem. Soc.*, 1912, **34**, 1213—1229).—Whilst failing to prepare maltase from the yeast of Californian "steam beer," which is brewed at a higher temperature and with more extensive aeration than common lager beers, a ferment has been discovered which is very active at 70° towards dextrose, polyphenols, and lactates. It manifests itself in the case of dextrose by a rapid darkening of the mixture, a strongly acid reaction, a gradual formation of a carbonaceous solid

deposit, and the development of a caramel-like odour, but it causes no formation of gas or of alcohol. It accelerates the oxidation of quinol, and traces of manganese sulphate intensify this activity.

This yeast glucase may be extracted from yeast powder, which is best obtained by treating the cells with ethyl alcohol. The aqueous extract of this powder is prepared at 70°, and is very stable under sterile conditions, whilst boiling does not destroy its activity. Repeated precipitation with alcohol results in a brittle mass, which still contains many gum-like substances, and is not so strong a ferment. Many of the properties of the glucase have been studied; it gives a strong pyrrole reaction (see Neuberg, Abstr., 1905, ii, 127), but it does not act as a peroxydase towards dextrose, neither does it contain tyrosinase. Among the transformation products of dextrose, pentose and formaldehyde were ascertained, but the acids have not been identified.

Since it is an oxidative ferment, which at the same time acts on dextrose, it is classed with zymase, with which, however, it is not identical, apart from the oxydases and hydrolytic ferments, among the "Gärungsenzyme" of Euler. J. C. W.

The So-called Terpentinphosphorous Acid. ERNST SIEBURG (*Biochem. Zeitsch.*, 1912, **43**, 280—314).—The author shows that the waxy substance obtained by dissolving phosphorus in *l*-pinene in the presence of air is a monobasic acid. The substance was obtained by expressing from the waxy-mass the excess of pinene, and dissolving it in sodium hydroxide solution, from which it was precipitated by excess of hydrochloric acid. It was then dissolved in chloroform, the chloroform solution was repeatedly washed with water, and then dried over sodium sulphate. On evaporating off the chloroform, the substance used for investigation was obtained. Its analyses agree with the formula $C_{10}H_{17}O_3P$, and the sodium, lithium, lead, and barium salts were obtained and analysed. It appears to be a derivative of hypophosphorous acid. On gentle oxidation (by bromine water, etc.), it is converted into a phosphorous acid derivative of terpene. It is practically non-toxic, as demonstrated by numerous experiments on fowls, rabbits, and dogs, and is oxidised in the organism, being excreted in the urine in the form of an acid, $C_{10}H_{17}PO(OH)_2$, a terpinolphosphoric acid. No glycuronate was found. S. B. S.

Methylated Diaminodihydroxyarsenobenzenes. ALFRED BERTHEIM (*Ber.*, 1912, **45**, 2130—2136).—The following substances have been prepared for the purpose of tracing the change of the biological properties of salvarsan by the successive introduction of methyl groups into the amino-groups. Since the direct methylation of salvarsan is a complicated process, its methyl derivatives have been obtained as follows.

3-*Methylamino-4-hydroxyphenylarsinic acid*,

$$NHMe\cdot C_6H_3(OH)\cdot AsH_2O_3,$$

m. p. 263—263·5° (decomp.), is prepared from 3-amino-4-hydroxyphenylarsinic acid and methyl sulphate (0·5 mol.) in alkaline solution at the ordinary temperature. The crystals contain $\frac{1}{2}H_2O$. By reduc-

tion with alkaline sodium hyposulphite at about 50°, the acid yields 3 : 3′-*dimethylamino*-4 : 4′-*dihydroxyarsenobenzene*,

$$As_2[C_6H_3(OH)\cdot NHMe]_2,$$

the *dihydrochloride* of which is a yellow, microcrystalline powder, resembling salvarsan in many respects, but differing from it by developing a brownish-orange coloration and no precipitate with an hydrochloric acid solution of *p*-dimethylaminobenzaldehyde. 3-*Dimethylamino*-4-*hydroxyphenylarsinic acid*, $NMe_2\cdot C_6H_3(OH)\cdot AsH_2O_3$, m. p. 119—121° (decomp.), obtained from 3-amino-4-hydroxyphenylarsinic acid and methyl sulphate (1 mol.) in alkaline solution at the ordinary temperature, is reduced by alkaline sodium hyposulphite to 3 : 3′-*bis-dimethylamino*-4 : 4′-*dihydroxyarsenobenzene*, $As_2[C_6H_3(OH)\cdot NMe_2]_2$, the *dihydrochloride* of which is a yellowish-white powder. By repeated treatment with *N*-sodium hydroxide and methyl iodide at the ordinary temperature, 3-amino-4-hydroxyphenylarsinic acid in the presence of methyl alcohol is converted into a mixture which yields 4-*hydroxyphenylarsinic acid*-3-*trimethylammonium hydroxide*,

$$OH\cdot NMe_3\cdot C_6H_3(OH)\cdot AsH_2O_3,$$

and its *iodide* by treatment with acetic acid. The former, which is obtained pure in glistening prisms by crystallising the mixture from water, has m. p. 262—264° (decomp.), loses H_2O at 110—114° with the formation of an inner *anhydride*, and is reduced by alkaline sodium hyposulphite to salts of 4 : 4′-*dihydroxyarsenobenzene*-3 : 3′-*bistrimethylammonium hydroxide*, $As_2[C_6H_3(OH)\cdot NMe_3X]_2$.

[With Frida Leupold.]—All three methylated diaminodihydroxyarsenobenzenes are decidedly more toxic than salvarsan itself, the dimethyl and tetramethyl compounds being ten times, and the hexamethyl compound three to five times, as poisonous.

The introduction of the methyl groups causes an extraordinary deterioration in the curative effect of the substance. The ammonium compound has no effect at all. The dimethyl compound, in a quantity equal to half the lethal dose, renders the animal free from trypanosoma only for a few days, whilst the tetramethyl compound kills a sick animal when given in a quantity equal to half the lethal dose for a healthy animal, and has no effect on the trypanosoma when given in one-third of the lethal dose. C. S.

New Class of Organo-Silicon Compounds which Evolve Hydrogen. Geoffrey Martin (*Ber.*, 1912, 45, 2097—2106).—By the action of Grignard reagents on silicon tetrachloride under definite conditions, complex organic silicon compounds are obtained, which are insoluble in ether, in other organic solvents, and in dilute mineral acids, and evolve the same amount of hydrogen by heating at 400—500° or by solution in dilute alkali hydroxides. When kept for some time or when boiled with acids, the substances are converted into others which no longer evolve hydrogen by solution in alkalis, but still evolve hydrogen when heated, the amount of hydrogen produced being the same as that obtained by the solution of the original substance in alkali.

The peculiar behaviour of these substances is explained by assuming that the original compounds contain one or more of the groups

$$OH\cdot\overset{\cdot}{\underset{\cdot}{Si}}\cdot\overset{\cdot}{\underset{\cdot}{Si}}\cdot OH.$$

By solution in potassium hydroxide, each of these groups changes into $OK\cdot\overset{\cdot}{\underset{\cdot}{Si}}\cdot O\cdot\overset{\cdot}{\underset{\cdot}{Si}}\cdot OK$, with the evolution of one molecule of hydrogen; the quantity of hydrogen evolved, therefore, is a measure of the number of directly linked silicon atoms in the substance. When the substance is kept or boiled with acids, the group changes to $>SiH\cdot O\cdot\overset{\cdot}{\underset{\cdot}{Si}}\cdot OH$. The new compound, therefore, no longer evolves hydrogen by treatment with potassium hydroxide, because it does not contain directly linked silicon atoms; by heating, however, one molecule of hydrogen is evolved in consequence of the change

$$>SiH\cdot O\cdot\overset{\cdot}{\underset{\cdot}{Si}}\cdot OH \rightarrow >Si{<}^{O}_{O}{>}Si< + H_2.$$

Silicon tetrachloride (1 mol.) in dry ether is treated with magnesium (2 atoms) and ethyl bromide (1 mol.). The product is washed with ether and decomposed by water. After being washed with water, alcohol, and ether, the final *product* is obtained as a yellow powder, which is found to have the composition $Si_4H_6O_7Et_2$, and to contain 3 pairs of directly linked silicon atoms by means of the amount of hydrogen evolved by solution in potassium hydroxide. By acidifying the alkaline solution, a white *substance*, $Si_4H_2O_8Et_2$, is obtained.

In a similar manner, magnesium α-naphthyl bromide (1 mol.), silicon tetrachloride (7 mols.), and magnesium (1 atom) yield a *substance*, $Si_6H_5O_{12}\cdot C_{10}H_7$, containing two Si·Si groups; bromobenzene (1 mol.), magnesium (2 atoms), and silicon tetrachloride (1 mol.) yield a *substance*, $Si_4H_8O_8Ph$, containing one Si·Si group (the ethereal extract contains a substance which is decomposed by water, forming a *substance*, $Si_7H_5O_{11}Ph_3$, containing four Si·Si groups); magnesium benzyl chloride and silicon tetrachloride yield a *substance* which is unstable, evolves hydrogen by treatment with hot water, and changes in three weeks to a *substance*, $Si_8H_3O_{16}(CH_2Ph)_3$, which is not easily soluble in potassium hydroxide (the ethereal extract contains a substance which is decomposed by water, yielding a *substance*,

$$Si_7H_3O_{14}(CH_2Ph)_3,$$

and a second *substance*, $Si_3HO_6\cdot CH_2Ph$).

The constitutions of the preceding compounds and also the changes they undergo by keeping or by treatment with acids or alkalis are represented by provisional formulæ. C. S.

Organic Chemistry.

Action of Aqueous Solutions of Acids on Olefines. ARTHUR MICHAEL and ROGER F. BRUNEL (*Amer. Chem. J.*, 1912, 48, 267—279. Compare Abstr., 1909, i, 197).—It has been stated by Scheschukoff (Abstr., 1886, 680) that when *iso*butylene is passed into aqueous hydriodic acid, saturated at 0°, *tert.*-butyl iodide is produced until the acid has attained the concentration represented by $2HI + 11H_2O$ (D = 1·7), and at this point the reaction ceases, the *iso*butylene being no longer absorbed. It has now been found that these observations are not correct. The absorption of the hydrocarbon does not cease when the acid has D 1·7 although it decreases considerably. The rate of formation of *tert.*-butyl iodide is, however, no longer a criterion for the rate of absorption of the gas, as part of the hydrocarbon dissolves with production of the soluble tertiary carbinol.

Similar experiments have been made with trimethylethylene and hydrobromic acid, which have shown that 9·66*N*-acid yields chiefly the bromide, whilst a solution more dilute than 5·54*N* gives carbinol only; intermediate concentrations yield mixtures of the two compounds. The mechanism of the reaction is discussed, and it is shown that it is probable that the hydrocarbon reacts with both the water and the acid simultaneously. At a concentration equivalent to $HBr + 8H_2O$, the amylene reacts with amounts of water and acid in the same ratio. It is suggested that this may be explained by assuming the formation of a "polymolecule," such as C_5H_{10},HBr,H_2O, and theoretical evidence is adduced for expecting that the decomposition of x "polymolecules" would proceed with the production of $x/2$ mols. of haloid and carbinol respectively, whilst a system containing a larger or smaller proportion of the hydrogen bromide should give a corresponding increase or decrease in the amount of haloid produced.

The combination of water with olefines resembles the hydrolysis of methyl acetate and sucrose, and it was therefore considered of interest to ascertain whether the catalytic effects of acids stand in the same relation to each other in the first case as in the latter reactions. The velocity of solution of trimethylethylene and *iso*butylene in dilute solutions of acids was therefore determined. It was found that the order in which hydriodic, hydrobromic, and hydrochloric acids in dilute solutions exert a catalytic influence in inducing the addition of water to the amylene is the same as that of the facility of addition of the acids themselves to unsaturated hydrocarbons, and also as that of the reactivity of these acids in converting carbinols into haloids. E. G.

Preparation of Isoprene and Erythrene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247144 and 247271. Compare Abstr., 1888, 1292, and this vol., i, 742).—I. The conversion of β-methylpyrrolidine into isoprene as recorded by Euler has led to the following method of preparing both isoprene and erythrene. Keto-

methylbutanol, $CH_3·CO·CHMe·CH_2·OH$, was converted into its *oxime* b. p. 144°/20 mm., and this reduced to the *base*,

$$CH_3·CH(NH_2)·CHMe·CH_2·OH,$$

a viscous oil, b. p. 96°/18·5 mm., which was condensed by the action of halogen acids to 2 : 3-*dimethyltrimethylenimine*,

$$CH_3·CH<\begin{matrix}CHMe\\CH_2\end{matrix}>NH,$$

an oil, b. p. 88°. This compound on exhaustive methylation furnished 2 : 3-*dimethyltrimethylendimethylammonium iodide*,

$$CH_3·CH<\begin{matrix}CHMe\\CH_2\end{matrix}>NMe_2I,$$

m. p. 191°, which was converted by silver oxide into the quaternary *base*, and on distillation furnished *dimethyl-αβ-dimethylallylamine*, $CH_2:CMe·CHMe·NMe_2$, a colourless oil, b. p. 105—106°, with an odour of piperidine, which after conversion into the quaternary *ammonium iodide* (leaflets, m. p. 138—140°) can be readily converted by alkali or alkaline-earth hydroxides into isoprene and trimethylamine.

The preparation of erythrene by a similar series of reactions from ketobutanol, $CH_3·CO·CH_2·CH_2·OH$, furnished the following intermediate compounds: the *oxime*, $CH_3·C(:NOH)·CH_2·CH_2·OH$, b. p. 125—130°/20 mm.; the hydroxy-*base*, b. p. 82—85°/19 mm.; 2-*methyltrimethylenimine*, $CH_2<\begin{matrix}CHMe\\CH_2\end{matrix}>NH$, b. p. 75°; *dimethyl-α-methylallylamine*, $CH_2:CH·CHMe·NMe_2$, a colourless oil, b. p. 90—93°, with an odour of coniine, and *trimethyl-α-methylallylammonium chloride*,

$$CH_2:CH·CHMe·NMe_3Cl,$$

a crystalline, colourless, hygroscopic mass.

II. When the quaternary ammonium haloids of the hydroxy-bases, $CH_3·CH(NH_2)·CH_2·CH_2·OH$ and $CH_3·CH(NH_2)·CH·CH_3·CH_2OH$, are heated with halogen acids, the hydroxyl groups are replaced by a halogen atom, and the halogenated bases thus obtained are readily converted by alkali or alkaline-earth hydroxides into isoprene or erythrene respectively; the *compounds* $Br·CH_2·CHMe·CHMe·NMe_3Cl$ and $Br·CH_2·CH_2·CHMe·NMe_3Cl$ are syrups. F. M. G. M.

Course of the Intramolecular Transformations of Alkyl Bromides. II. ARTHUR MICHAEL and FRITZ ZEIDLER (*Annalen*, 1912, **393**, 81—111. Compare Abstr., 1911, i, 250).—The authors have undertaken experiments in order to ascertain whether the presence of impurities may not be the cause of the discordant results obtained by different observers during investigations of the transformation of *iso*butyl bromide into the tertiary isomeride (*loc. cit.*). It has been found that the majority of the methods of preparing alkyl bromides do not yield pure products.

The *iso*butyl alcohol employed, details of the purification of which are given, had b. p. 107·7—107·8°/761·4 mm. for one sample and 107·2—107·3°/750·5 mm. for another.

*iso*Butyl bromide prepared by Norris's method (Abstr., 1907, i, 1034) contains di*iso*butylene, which cannot be removed by distillation. Such *iso*butyl bromide yields only 1·36% of *tert.*-butyl bromide by heating for three hours at 141° in the apparatus described by Michael

and Zeidler (this vol., i, 2). After removing the di*iso*butylene by 2% potassium permanganate, the thus purified *iso*butyl bromide has a more constant b. p., 91·3—91·7°/758·1 mm., and yields 30·73% and 45·68% of tertiary bromide after heating for three and ten hours respectively at 141°. When Norris's *iso*butyl bromide is freed from di*iso*butylene by treatment with bromine and subsequent fractionation, the purified *iso*butyl bromide has b. p. 91·6—92·1°/763·8 mm., and shows a still greater velocity of transformation, yielding 39·40% of tertiary bromide after three hours at 141°. By adding 1—2% of di*iso*butylene to this purified *iso*butyl bromide, its velocity of transformation is diminished enormously, only about 10% of tertiary bromide being formed after three hours at 141°.

*iso*Butyl bromide, obtained from *iso*butyl alcohol, potassium bromide, and sulphuric acid, contains a considerable amount of di*iso*butylene, and yields only 1½% of the tertiary bromide by heating at 141° for three hours.

A purer product is obtained by saturating *iso*butyl alcohol with hydrogen bromide at 0° and subsequently heating at 100°. The *iso*butyl bromide, after fractionation, has b. p. within 0·1°, and yields 12—24% of the tertiary bromide at 141°; the transformation then ceases, but at 262° more than 75% of the tertiary bromide is produced. Several variations of the preceding method have been tested in order to obtain an *iso*butyl bromide which is easily transformed into the tertiary bromide. Finally, the following process is adopted. Hydrogen bromide, prepared from purified bromine, purified red phosphorus, and water, is washed by moist red phosphorus and by ferrous bromide solution, and is then absorbed in water. By distillation the solution gave an acid, b. p. 125—126°, which is free from hydrogen phosphide. This acid is used for the absorption of further quantities of hydrogen bromide, and by heating the saturated solution, very pure hydrogen bromide is obtained. Equal volumes of *iso*butyl alcohol and hydrobromic acid, b. p. 125—126°, are saturated with hydrogen bromide and heated in a sealed vessel at 75—80° for two hours. The resulting *iso*butyl bromide (95% yield) yields after purification and careful fractionation a sample, b. p. 91·85—92°/762·2 mm., which gives 73·28% of tertiary bromide after one hour at 141° and 71·89% after one hour at 262°. By mixing this pure *iso*butyl bromide with 2·66% of di*iso*butylene, 3·74% of *tert.*-butyl alcohol, and 2·31% of *iso*butyl alcohol, the amounts of *tert.*-butyl bromide obtained after one hour at 141° are 4·94%, 0%, and 7·06% respectively.

The limit of the transformation of *iso*butyl bromide into *tert.*-butyl bromide attained in these experiments is about 76%. The same limit is attained from the other side. Pure *tert.*-butyl bromide, b. p. 72·8—73·1°/762·85 mm. and 71·6—72·0 (two samples), prepared from purified *tert.*-butyl alcohol and hydrobromic acid, D 1·78, yields 23·88% and 23·18% respectively of *iso*butyl bromide after one hour at 262°, the amount and the velocity of the transformation being much smaller at lower temperatures. A sample of *tert.*-butyl bromide, prepared from *iso*butylene and concentrated hydrobromic acid by Roozeboom's method and having b. p. 72·5—72·6°/747·3 mm., and containing 100% of the tertiary bromide, yielded, curiously enough,

only 19·56% of *iso*butyl bromide after two hours at 262°; apparently, the transformation of the tertiary bromide is slower the purer it is.

*iso*Butyl chloride is transformed by heating into the tertiary chloride very much more slowly than *iso*butyl bromide is changed to the tertiary bromide. A sample, prepared by saturating *iso*butyl alcohol with pure hydrogen chloride at 0° and then heating at 120° in a sealed vessel, had b. p. 68·8—69·2°/769·2 mm. after purification, and yielded 0% of the tertiary chloride after one hour at 184°, and only 7·94% after six hours at 306°.

The deductions drawn by Brunel from his experiments (Abstr., 1911, ii, 974) are adversely criticised. C. S.

Pyrogenic Decomposition of Methyl Alcohol by means of the Electric Current. WALTHER LÖB (*Zeitsch. Elektrochem.*, 1912, **18**, 847—850).—The method of experiment has already been described (compare Abstr., 1901, ii, 371; 1902, i, 3). A nickel wire of 0·3 mm. diameter was electrically heated to about 700°, and its action on methyl alcohol investigated. In the first series of experiments a mixture of methyl alcohol and water was used, and it was found that the gaseous products were almost exclusively formaldehyde and hydrogen, according to the equation: $CH_3{\cdot}OH = CH_2O + H_2$. When mixtures of methyl alcohol and benzene were used, the same products were obtained, with traces only of diphenyl; owing to the absence of water, the formaldehyde partly condensed to paraformaldehyde. At rather higher temperatures, formaldehyde decomposes into carbon monoxide and hydrogen. In the presence of ammonia, the pyrogenic decomposition of methyl alcohol yields a considerable proportion of hexamethylenetetramine. G. S.

Chemical Action of Methyl and Ethyl Alcohols. HANS VON LIEBIG (*Arch. Pharm.*, 1912, **250**, 403—413).—In medicinal and in plant chemistry, methyl and ethyl alcohols are the solvents which are most commonly used for extraction or crystallisation. Since the assumption is generally made that these alcohols have no chemical action on the substance extracted by, or crystallised from, them, the author calls attention to some instances in which the assumption is untenable, particularly in the resorcinolbenzein and fluorescein series (Abstr., 1907, i, 45; this vol., i, 378). The alcohols have both a hydrolysing and etherifying action. The constitutions of the products are discussed.

The conversion of phytylchlorophyllide into ethylchlorophyllide by ethyl alcohol may be due to the chemical action of the alcohol, not to the action of the enzyme chlorophyllase, as stated by Willstätter. C. S.

The History of Alcohol and its Name. EDMUND O. VON LIPPMANN (*Zeitsch. angew. Chem.*, 1912, **25**, 2061—2065).—Contrary to the usual statement, alcohol was unknown to the Arabian chemists. The process of distillation was also unknown in Asia. The discovery of alcohol probably took place in Italy. It is first mentioned in an Italian work of the ninth or tenth century. C. H. D.

Basic Properties of Oxygen. Two-Component Systems of the Halogen Hydrides with Organic Substances Containing Oxygen. O. MAASS and DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1912, **34**, 1273—1290).—It is pointed out that the compounds formed by the combination of halogens and halogen hydrides with organic substances containing oxygen may be regarded as quite distinct from the so-called molecular compounds, such as salts containing water, alcohol, or ether of crystallisation.

In an earlier paper (Abstr., 1911, i, 256), an account has been given of two-component systems of ether with hydrogen bromide, chlorine, and bromine. The existence of two compounds of ether and hydrogen bromide is now confirmed, and it is shown that an excess of ether favours the formation of the monohydrobromide, and an excess of hydrogen bromide that of the dihydrobromide.

The systems chloroform–hydrogen bromide and chloroform–hydrogen chloride have been studied in comparison with the oxygen compounds. No compound is formed in either case, but the f. p. of each component is lowered by the addition of the other until the eutectic point is reached.

The systems toluene–hydrogen bromide and toluene–chlorine show the formation of *compounds*, C_7H_8,HBr and C_7H_8,Cl_2, but these are very unstable as compared with the oxonium complexes.

Methyl ether yields with hydrogen bromide the *compound*,

$$(CH_3)_2O,HBr,$$

m. p. $-13°$, with hydrogen iodide the *compound*, $(CH_3)_2O,HI$, m. p. $-22°$, and with hydrogen chloride the *compounds*, $(CH_3)_2O,HCl$, m. p. $-96°$, and $(CH_3)_2O,3HCl$ or $(CH_3)_2O,4HCl$, m. p. $-102°$.

Methyl alcohol and hydrogen bromide give the *compound*,

$$CH_3{\cdot}OH,HBr,$$

m. p. $-12°$, in the formation of which much heat is developed. With bromine, the existence of the *compound*, $CH_3{\cdot}OH,Br$, m. p. $-66°$, is indicated.

Ethyl alcohol yields with hydrogen bromide and bromine the *compounds*, $C_2H_5{\cdot}OH,HBr$, m. p. $-30°$, and $C_2H_5{\cdot}OH,Br$, m. p. $-58°$. In order to explain the constitution of the latter substance, the formula must be doubled and the compound represented as $\overset{C_2H_5}{\underset{H}{}}{>}O{:}Br{\cdot}Br{:}O{<}\overset{C_2H_5}{\underset{H}{}}$.

Acetone gives the *compounds*, $COMe_2,HBr$, m. p. $-4°$, $COMe_2,Br_2$, m. p. $-8°$, and $COMe_2,Cl_2$, m. p. $-54°$. The constitution of the halogen compounds is probably best represented by the formula

$$COMe_2{:}X{\cdot}X{:}X{\cdot}X{:}OCMe_2.$$

Ethyl acetate yields the *compounds* $CH_3{\cdot}CO_2Et,HBr$, m. p. $-36°$, $2CH_3{\cdot}CO_2Et,5HBr$, m. p. $-52°$, $CH_3{\cdot}CO_2Et,4HBr$, m. p. $-57°$, $CH_3{\cdot}CO_2Et,3Br$, m. p. $-35°$, and $CH_3{\cdot}CO_2Et,3Cl$, m. p. $-68°$.

All the halogen hydride complexes have m. p.'s much above those of either constituent. The compounds are formed with the development of an amount of heat equal to, or greater than, that liberated when a halogen acid is neutralised by potassium hydroxide. The compounds, either in the fused state or in a solution of either constituent, readily conduct the electric current.

The chlorine and bromine compounds are formed with the development of but little heat, and are non-conducting. Their constitutions are doubtful, but it is evident that they must differ radically from those of compounds ionised in solution. E. G.

Ethyl Ether. GEORG KASSNER (*Arch. Pharm.*, 1912, **250**, 436—447).—Instances of the spontaneous explosion of ether by heating have been placed on record. A sample of ether, a portion of which exploded violently when it was being sealed in a Dumas bulb in the determination of its vapour density, has been carefully examined by the author. It contained traces of hydrogen peroxide and acetaldehyde, and a relatively large amount of vinyl alcohol. The author is of opinion that the explosion was caused by the presence of an organic peroxide (ethyl peroxide) which had been produced by autoxidation. C. S.

Commercial Sodium Glycerophosphates. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 350—352. Compare Abstr., 1911, i, 774).—The author has examined several commercial sodium glycerophosphates, and finds them to have the same composition as Poulenc's product. R. V. S.

Bromination of Aliphatic Acids. CLARENCE SMITH and WILLIAM LEWCOCK (*Ber.*, 1912, **45**, 2358—2359).—The theory of the bromination of aliphatic acids advanced by Aschan (this vol., i, 599), involving successive enolisation of the acid (or acid chloride, in practice), addition of the halogen, and elimination of halogen hydride, is supported by the behaviour of *iso*butyryl chloride towards bromine. When heated together in equal molecular quantities at 100° for four hours, the *iso*butyryl chloride is converted almost entirely into α-bromo*iso*butyryl bromide. In accordance with the theory, α-bromo-*iso*butyryl chloride is unaffected by bromine at 100°. C. S.

Saponification of Triglycerides. V. FORTINI (*Chem. Zeit.*, 1912, **36**, 1117).—It has been held by some authors that in the saponification of fats, the triglycerides are immediately hydrolysed to the fatty acids and glycerol, whilst others have asserted that the hydrolysis takes place in steps, diglycerides and monoglycerides being formed (compare Lewkowitsch, Proc., 1899, **15**, 190; Marcusson, Abstr., 1906, i, 924; Kremann, Abstr., 1906, ii, 731; Stritar, Abstr., 1908, ii, 677, 1021; Grün and Corelli, this vol., i, 409). The results now recorded support the second view.

The curves obtained by plotting (1) quantity of triglyceride hydrolysed against time, or (2) acetyl number against time, each consist of three parts corresponding with (*a*) formation of diglycerides, (*b*) formation of monoglycerides, (*c*) formation of free fatty acids. The experiments were made by saponifying triolein with alkali hydroxide in alcohol at 20°. T. A. H.

Oil from the Seeds of Jatropha mahafalensis. HENRI BIMAR (*Bull. Soc. chim.*, 1912, [iv], **11**, 914—915).—The seeds contain 75% of their weight of kernels, and the latter yield on extracting with

carbon disulphide 60%, or under pressure 44·5%, of an amber-tinted slightly fluorescent oil, D^{15} 0·9213, n_D^{20} 1·4648, titre 21°, saponification number 194, acid number 17·6, iodine value 111·8, acetyl number 17, which dries in twenty-six hours at 50°. The mixed ethyl esters of the fatty acids gave the following fractions: (1) b. p. 180—185°/5 mm., saponification number 186, iodine value 98; (2) b. p. 188—190°/5 mm., saponification number 186, iodine value 105; (3) b. p. 193—195°/5 mm., saponification number 184, iodine value 112, indicating that the fat contains linoleic acid and no acids of lower molecular weight than palmitic acid. T. A. H.

Purification of Ammonium Hydrogen Salts of α-Hydroxy-acids. RICHARD ESCALES and HANS KOEPKE (D.R.-P. 247240).—The readiness with which lactic and glycollic acids lose water when heated has rendered their purification difficult; it is now found that the ammonium hydrogen salts can be distilled in a vacuum without decomposition. Ammonium hydrogen glycollate has b. p. 160°/10 mm., and crystallises on cooling, whilst the corresponding lactate has b. p. 140°/10 mm., and remains a viscous syrup. F. M. G. M.

β-Aldehydopropionic Acid. CARL D. HARRIES (*Ber.*, 1912, **45**, 2583—2585).—In a recent communication, Carrière (this vol., i, 410) gives values for the m. p. of various derivatives of β-aldehydopropionic acid, differing considerably for those previously obtained by the author (Abstr., 1909, i, 132, 133, 364; compare also Langheld, *loc. cit.*, i, 557). The latter has therefore repeated his earlier work and fully confirmed the results already given. β-Aldehydopropionic acid has b. p. 143—145°/16—20 mm., and is transformed after two days into a solid bimolecular form, m. p. 147°, and not a termolecular form of m. p. 167° as stated by Carrière.

The *p*-nitrophenylhydrazone, after repeated crystallisation from water, has m. p. 177°. F. B.

The Chemistry of Thorium. OTTO HAUSER and FRITZ WIRTH (*Zeitsch. anorg. Chem.*, 1912, **78**, 75—94).—Ordinary thorium oxalate,

$$Th(C_2O_4)_2,6H_2O,$$

is much less soluble in sulphuric acid than the oxalates of the tervalent earths (Abstr., 1908, ii, 778). The solubility in hydrochloric acid first increases and then falls rapidly, owing to the formation of the compound $3Th(C_2O_4)_2,ThCl_4,20H_2O$ (compare Wyrouboff and Verneuil, Abstr., 1899, ii, 598). In contact with dilute acids the oxalate is gradually converted into the stable modification, which forms tetragonal crystals. Both modifications yield the dihydrate over sulphuric acid, the crystalline hexahydrate retaining its crystalline form during dehydration, but exhibiting optical anomalies. Another hydrate, $4Th(C_2O_4)_2,3H_2O$, is obtained on heating.

The solution of thorium oxalate in ammonium oxalate solution at 25° takes place in two stages: $2Th^{\cdot\cdot\cdot\cdot} + 5C_2O_4'' = [Th_2(C_2O_4)_5]''$ and $Th^{\cdot\cdot\cdot\cdot} + 3C_2O_4'' = [Th(C_2O_4)_3]''$. The stable tetrahydrate is always formed by the hydrolysis of the complex salts. The salts

$$Th_2(C_2O_4)_5(NH_4)_2,7H_2O$$

and $Th(C_2O_4)_3(NH_4)_2,3H_2O$ have been prepared. The former crystallises in thin laths, whilst the latter, the limits of stability of which have been determined, has only been obtained in an amorphous form. The complex salts are only stable in presence of a large excess of ammonium oxalate, and the precipitation by acids is a function both of the concentration of the oxalate and of the acid. It is rather remarkable that the solubility of ammonium oxalate in water is increased five times by the addition of thorium oxalate. C. H. D.

The Walden Inversion. GEORGE SENTER (*Ber.*, 1912, **45**, 2318—2322).—With reference to a preliminary paper by Holmberg with the same title as above (compare this vol., i, 603), in which it is shown that when an aqueous solution of the sodium salt of *l*-monobromosuccinic acid is heated the Br′ ion concentration increases at first more rapidly than the free acid, the author states that he made a similar observation with sodium bromoacetate solution one and a-half years ago, and some of the conclusions drawn from the detailed investigation have already been published (compare Proc., 1911, **27**, 153). The phenomenon is only observed in concentrated solution. The suggestion of Holmberg that it can be accounted for on the theory of the intermediate formation of lactones is criticised. The detailed results will be published later. G. S.

Symmetric and Asymmetric Acid Dichlorides. ERWIN OTT (*Annalen*, 1912, **392**, 245—285).—The author approaches the problem of the constitution of acid dichlorides, such as succinyl chloride and phthalyl chloride (compare Scheiber, this vol., i, 559, 701), by means of criteria obtained by a comparative examination of maleinoid and fumaroid acid dichlorides. These criteria indicate that maleinoid chlorides have a lactonoid constitution, whilst fumaroid chlorides are acyclic and symmetric.

The criteria are the following. Fumaroid and maleinoid acid dichlorides exhibit extraordinarily great difference in their velocity of reaction in a homogenous system. All fumaroid dichlorides in *N*/50-solution in ether or benzene react momentarily with a primary base, such as aniline, to give the calculated amount of aniline hydrochloride. All maleinoid chlorides do not thus react under the same conditions; only after many days is the separation of the aniline hydrochloride complete. Thus chlorofumaryl chloride and dibromofumaryl chloride react instantly, whilst chloromaleyl chloride and dibromomaleyl bromide require sixteen days and fifty hours respectively. The same differences are observed in the rates of ester formation between the four acid dihaloids and methyl alcohol, the two symmetric compounds yielding 100% hydrogen chloride instantly, whilst the asymmetric dihaloids require many hours.

This difference in behaviour is not explicable by formulating maleinoid and fumaroid acid dihaloids as acyclic isomerides differing only in the spatial distribution of the ·COX-groups, because the examination of *s*-*o*-phthalyl chloride (see below) shows that the mere spatial approximation of two ·COCl-groups is insufficient to cause a diminution of the reaction velocity. Assuming what is now very generally

accepted, that acyl haloids owe their reactivity, not to direct substitution, but to addition, followed by elimination, the preceding differences are satisfactorily explained by formulating maleinoid dihaloids as cyclic ketones, $\left.\begin{matrix}\cdot C\cdot CCl_2\\ \|\\ \cdot C—CO\end{matrix}\right>O$, because an acyl halogen atom is no longer present. The reaction with aniline is then due, either to a transformation of the cyclic dichloride into the acyclic,

$$\left.\begin{matrix}\cdot C\cdot CCl_2\\ \|\\ \cdot C—CO\end{matrix}\right>O \longrightarrow \begin{matrix}\cdot C\cdot COCl\\ \|\\ \cdot C\cdot COCl\end{matrix},$$

or, better, by the scheme:

$$\left.\begin{matrix}\cdot C—CO\\ \|\\ \cdot C\cdot CCl_2\end{matrix}\right>O + NH_2Ph \longrightarrow \begin{matrix}C\cdot C(OH)\cdot NHPh\\ \|\quad >O\\ C\cdot CCl_2\end{matrix} \longrightarrow \begin{matrix}\cdot C\cdot CO\cdot NHPh\\ \|\\ \cdot C\cdot COCl\end{matrix} + HCl.$$

Both explanations account for the production of the symmetric dianilide, but the latter is preferable, because, according to the former, the velocity of reaction of maleinoid dichlorides should be proportional to the stability of the γ-lactone ring, which is found not to be the case.

A second criterion is the colour of the aluminium chloride compounds. Chlorofumaryl chloride and aluminium chloride form a yellow mass, m. p. about 50°, from which chlorofumaryl chloride is regenerated by water at 0°. By warming, however, the mass becomes reddish-brown, and then has m. p. about 100° and yields chloromaleyl chloride by treatment with ice water. The reddish-brown substance is the aluminium chloride compound of chloromaleyl chloride, and its more intense colour is accounted for if chloromaleyl chloride has the cyclic ketonic structure, since the aluminium chloride compounds of cyclic ketones are intensely coloured. At 180—230°, the aluminium chloride compound of chloromaleyl chloride decomposes into carbon monoxide, hydrogen chloride, $\alpha\beta$-dichloroacrylyl chloride, and carbonyl chloride; the formation of the last substance is taken as evidence of the constitution, $\left.\begin{matrix}CCl\cdot CCl_2\\ \|\\ CH—CO\end{matrix}\right>O$, of chloromaleyl chloride.

A third criterion is the comparison of the degree of unsaturation of the ethylenic linking in chloromaleyl chloride and chlorofumaryl chloride respectively. In sunlight, the latter adds on 80—85% of the theoretical amount of bromine within five hours, whilst the addition of bromine to chloromaleyl chloride is not appreciable after a week. This difference is attributed to the presence of the two carbonyl groups in conjugated positions in chlorofumaryl chloride, and to their absence in the cyclic ketonic chloromaleyl chloride.

A fourth criterion is found in the molecular volume. A difference of 4·4 units should exist in the molecular volumes of isomeric maleinoid and fumaroid acid dihaloids if the former have a cyclic structure. This difference actually occurs in chloromaleyl chloride and chlorofumaryl chloride, which have molecular volumes 137·63 and 142·3 respectively at the b. p.

Since γ-lactones are frequently dimorphous, the existence of chloromaleyl chloride in two forms, m. p. 10·5—11° and 2·5—3° respectively (the more fusible changes to the less fusible merely by keeping for several weeks), is also indicative of its ketonic structure.

The application of these criteria to succinyl and phthalyl chlorides gives the following results, which on the whole indicate that the two chlorides have the symmetric constitution. They both react rapidly with aniline or with methyl alcohol. The molecular volume, 180·35, of phthalyl chloride at its b. p. agrees with that calculated, 180·0, for the acyclic formula; the molecular volume of succinyl chloride, 133·7, is intermediate between those, 136·0 and 131·6, calculated for the symmetric and asymmetric formulæ respectively. A conversion of succinyl chloride by aluminium chloride, corresponding with that of chlorofumaryl into chloromaleyl chloride, does not occur, but *s*-phthalyl chloride, which is conveniently obtained by slowly heating phthalic anhydride with a small excess of phosphorus pentachloride for half a day at 150° and finally at 250° until the phosphoryl chloride has distilled away, is converted, by dry aluminium chloride on the water-bath and subsequent treatment of the product with water at 0°, into an *isomeride*, m. p. 88—89°, b. p. 275·2°(corr.)/719·8 mm., large prisms, which is regarded as *as*-phthalyl chloride, $C_6H_4<\begin{matrix}CCl_2\\CO\end{matrix}>O$, on account of its slow velocity of reaction with aniline or methyl alcohol. By distillation, by prolonged heating on the water-bath, or in the presence of hydrogen chloride, the asymmetric chloride is converted into the ordinary symmetric chloride. Dibromofumaric acid is obtained in 92—93% yield, free from dibromomaleic acid, by leading air containing bromine vapour into an aqueous solution of acetylenedicarboxylic acid in darkness until the theoretical quantity of bromine has been absorbed. A suspension of dibromofumaric acid in petroleum is converted by phosphorus pentachloride and subsequent treatment with ice into *dibromofumaryl chloride*, $C_4O_2Cl_2Br_2$, b. p. 92·5°/9·5 mm. *Dibromomaleyl chloride*, m. p. 39°, b. p. 128°/14·5 mm., colourless leaflets, cannot be conveniently prepared in a similar manner, but is obtained by heating dibromofumaryl chloride at about 150° for four days or with aluminium chloride at 100° for a few hours. Dibromofumaryl chloride and aluminium bromide on the water-bath give a good yield of *dibromomaleyl bromide*, m. p. 55—57°, yellow leaflets, after treating the product with ice water. C. S.

Cholic Acid. I. HEINRICH WIELAND and FRIEDRICH JOSEF WEIL (*Zeitsch. physiol. Chem.*, 1912, **80**, 287—297).—On distillation of cholic acid in a vacuum (12 mm.) at 200—300°, a heavy, almost colourless oil distils over, and solidifies to a resin which consists mainly of triply unsaturated *cholatrienecarboxylic acid*, $C_{24}H_{34}O_2$. It crystallises in well formed plates, aggregated in large bunches; when heated it softens at 140°, m.p. 163—164°; $[\alpha]_D^{20} = -19·7°$. The acid dissolves in sulphuric acid with a deep yellow coloration; after a time the solution exhibits a green fluorescence. Bromine is at first decolourised, then hydrogen bromide is set free, and the acid solution becomes a golden-yellow.

In aqueous-alcoholic solution of the alkali salt, the acid is partly hydrogenated by the action of palladium-hydride, forming *choladienecarboxylic acid*, $C_{24}H_{36}O_2$. This crystallises similarly to the parent acid, but has m.p. 178°.

Reduction by means of palladium black and hydrogen in acetic acid suspension leads to *cholanecarboxylic acid*, $C_{24}H_{40}O_2$. It crystallises in radially arranged pointed crystals, m. p. 157·5°; $[\alpha]_D^{20}$ + 20·3°. This acid gives no coloration with sulphuric acid, and does not react with bromine. E. F. A.

Influence of Sunlight on the Synthesis of Alkaloid Bases by the Action of Alcoholic Ammonia on Aldehydes. IV. GIUSEPPE INGHILLERI (*Zeitsch. physiol. Chem.*, 1912, **80**, 64—72).—Sealed tubes containing formaldehyde, concentrated aqueous ammonia, and methyl alcohol were exposed to sunlight for seven months. Crystals of a base, $C_6H_8ON_2$ were produced, which decomposed without melting at 185°, formed a microcrystalline platinichloride, decomp. 220°, and gave a number of alkaloid reactions. From the portion of the reaction mixture insoluble in ether, three platinichlorides, containing 47·3, 26, and 25·5% of platinum respectively, were isolated. The two latter represent bases formed by the changes corresponding with the equations: $6HCHO - 5H_2O + 3NH_3$ and

$8HCHO - 7H_2O + 4NH_3$. E. F. A.

Methylglyoxal. JAKOB MEISENHEIMER (*Ber.*, 1912, **45**, 2635—2641. Compare Harries and Türk, Abstr., 1905, i, 413; Denis, Abstr., 1907, i, 997).—Methylglyoxal is most readily prepared by hydrolysing its acetal (Wohl and Lange, Abstr., 1908, i, 943) with *N*-sulphuric acid and extracting the residue, obtained by evaporation of its neutralised solution, with ether. After removal of the ether, the methylglyoxal is obtained as a yellow syrup, consisting of the termolecular form, from which the unimolecular variety is obtained by distilling it under diminished pressure and allowing the vapours to pass over anhydrous calcium chloride.

The unimolecular form is an intensely yellow, very mobile liquid, having a pungent odour. When heated under ordinary pressure, it begins to distil at 72°, forming a yellowish-green vapour; the greater part, however, is transformed into the termolecular form. At the ordinary temperature the transformation is complete in the course of eight to ten days.

When dissolved in water, the termolecular form passes into the unimolecular form (or its hydrate) in twenty-four hours. F. B.

The Action of Dilute Sodium Hydroxide on Glyceraldehyde and Dihydroxyacetone. MAX OPPENHEIMER (*Biochem. Zeitsch.*, 1912, **45**, 134—139).—In view of the assumed formation of glyceraldehyde and dihydroxyacetone as intermediary products in the degradation of dextrose to lactic acid, the relative rate of formation of this acid from these substances was investigated when they were submitted to the action of sodium hydroxide. From the results of experiments with *N*- and N/10-acid at room temperature and at 37°, the conclusion was drawn that lactic acid is formed most readily from dihydroxyacetone and least readily from the sugar. S. B. S.

Preparation of Pinacone from Acetone and Sodium. BADISCHE ANILIN- and SODA-FABRIK (D.R.-P. 248252).—The reduction

of acetone by sodium has previously furnished unsatisfactory yields of pinacone (Abstr., 1894, ii, 217); this reaction is now found to proceed smoothly in the presence of a liquid (such as ether) which is indifferent to sodium. F. M. G. M.

Styracitol. YASUHIKO ASAHINA (*Ber.*, 1912, **45**, 2363—2369. Compare Abstr., 1908, ii, 58; 1909, i, 288).—By treating a solution of styracitol in aqueous sodium carbonate with bromine, and subsequently acidifying and treating successively with sodium hydrogen sulphite, sodium acetate, and phenylhydrazine, an *osazone*, $C_{18}H_{20}O_3N_4$, m. p. 185°, thin leaflets, is obtained, which is optically active, and is not identical with Fischer and Zach's anhydroglucosazone.

By treatment in aqueous ferrous sulphate with 3% hydrogen peroxide and subsequently in acetic acid with phenylhydrazine, styracitol yields several products, among which *d*-phenylglucosazone has been identified. This substance is also produced when aqueous styracitol is oxidised by Caro's reagent at 0°.

Styracitol forms a *tetra-acetate*, prismatic crystals, m. p. 66—67°, or clusters of needles, m. p. 58°, which has $[\alpha]_D^{22}$ $-20\cdot86°$. Styracitol reacts readily with thionyl chloride on the water-bath to form a *disulphite*, $C_6H_8O_7S_2$, prismatic crystals, which is unaffected by boiling acetic anhydride. C. S.

Preparation of Mineral Acid Esters of Carbohydrates, the Corresponding Hydroxy-acids, and Higher Alcohols. CHEMISCHE WERKE VORM. HEINRICH BYK (D.R.-P. 247809).—*Calcium saccharophosphate* is obtained by treating a cooled suspension of sugar in calcium hydroxide with phosphoryl chloride, followed by the addition of chloroform:

$$2C_{12}H_{22}O_{11} + 2POCl_3 + 5CaO = 3CaCl_2 + H_2O + 2C_{12}H_{21}O_{10}\cdot O\cdot PO_3Ca;$$

it is a colourless powder, readily soluble in water, and does not give a precipitate with soluble copper or lead salts.

Calcium erythrosulphate is prepared from erythritol, calcium hydroxide, and chlorosulphonic acid, and a *compound* from calcium *d*-gluconate with phosphoryl chloride is also mentioned in the original. F. M. G. M.

New Form of Soluble Starch. AUGUSTE FERNBACH (*Compt. rend.*, 1912, **155**, 617—618).—By slowly pouring weak aqueous solutions of starch, not exceeding 2% in strength, into a large excess of pure acetone, a flocculent precipitate is obtained, which on filtering, extracting with more acetone, and drying in a vacuum yields a starch which is completely soluble in cold water, its solution giving a very pure blue colour with iodine. W. G.

Crystallised Polysaccharides from Starch. HANS PRINGSHEIM and ALFRED LANGHANS (*Ber.*, 1912, **45**, 2533—2546).—An extension of the work of Schardinger (Abstr., 1911, i, 181). The generic term *amylose* is suggested for the polysaccharides of the formula $(C_6H_{10}O_5)_n$.

Dextrin-β, which decomposes at 268°, is too sparingly soluble in water for accurate cryoscopy, but dextrin-α (tetra-amylose), decom-

posing at 292°, proves to have a molecular weight, $(C_6H_{10}O_5)_4$. Both forms are acetylated by acetic anhydride in the presence of zinc chloride, but scission of the molecules occurs at the same time; dextrin-α yields the *hexa-acetate* of a *diamylose*, needles (decomp. 151·5—152·5° (corr.), $[\alpha]_D^{24}$ +100·6° in acetic acid), whilst dextrin-β gives the *nona-acetate* of a *triamylose* (tablets, decomp. 142° (corr.), $[\alpha]_D^{24}$ +112·6° in acetic acid). Hydrolysis of these acetates by cold alcoholic potassium hydroxide produces respectively *diamylose* $(C_6H_{10}O_5)$ (decomp. about 300°, $[\alpha]_D^{24}$ +136·2° in water), which crystallises from water in needles with $2H_2O$, and *triamylose*, $(C_6H_{10}O_5)_3$, needles, crystallising with $4H_2O$, decomposing near 300°; $[\alpha]_D^{24}$ +151·8° in water. Crystallographic details of the above amyloses are given. D. F. T.

Fermentative Decomposition of the Hemicelluloses. I. A Trisaccharide as Intermediate Product of the Hydrolysis of Mannan. HANS PRINGSHEIM (*Zeitsch. physiol. Chem.*, 1912, **80**, 376—382).—By the action of a bacterial infusion on vegetable ivory nut turnings (Pringsheim, this vol., ii, 587), hydrolysis of the mannan takes place with the formation of mannose and a trisaccharide, probably a *trimannose*, identified by means of the *phenylosazone*, which crystallises in stellate aggregates of needles, decomp. 196° (corr.). It is completely fermented by most yeasts, but untouched by a yeast, No. 583, which is also without action on maltose, and may thus be separated from the monosaccharide. Emulsin hydrolyses it slowly, probably to a mixture of mono- and di-saccharide. E. F. A.

Acetylations in Ether Solutions. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1912, **34**, 1399—1409).—The reactions of acetyl chloride with organic bases are usually carried out by bringing the substances into direct contact, and the final products are generally the result of the decomposition of the original products by water or alkali. A study has now been made of the action of acetyl chloride on various bases in solution in dry ether. It has been found that in most cases a precipitate is produced, consisting of a mixture of the hydrochloride and acetyl chloride additive compound of the base, whilst the acetyl derivative remains dissolved in the ether. The results show that the acetyl chloride first unites with the base, thus: $RNH_2 + CH_3{\cdot}COCl \longrightarrow R(CH_3{\cdot}CO){\cdot}NH,HCl$. In the case of tertiary amines, an acetyl chloride additive product is invariably produced. With primary and secondary amines, it is sometimes the most abundant product, as in the case of benzylamine, but other substances are usually formed in accordance with the equations: $2RNH_2 + CH_3{\cdot}COCl \longrightarrow RNH_2,HCl + R(CH_3{\cdot}CO)NH$ and $2R_2NH + CH_3{\cdot}COCl \longrightarrow R_2NH,HCl + R_2(CH_3CO)N$.

When dry ammonia is passed into an ethereal solution of acetyl chloride, ammonium chloride and acetamide are formed. By the reaction of acetamide with acetyl chloride, diacetamide and acetamide hydrochloride, $2NH_2Ac,HCl$, are produced. Benzamide, under similar conditions, yields acetylbenzamide and its *hydrochloride*,

$$NHBzAc,HCl,$$

which is rapidly hydrolysed by water.

Ethylamine yields its hydrochloride together with those of mono- and di-acetylethylamine. *Diacetylethylamine* has b. p. 195—199°;

its *hydrochloride*, m. p. 65°, forms lustrous, hygroscopic needles. *iso*Amylamine gives its hydrochloride and that of its acetyl derivative. *Acetylisoamylamine* has b. p. 220—224°; its *hydrochloride* forms hygroscopic needles. With aniline, the hydrochloride and acetanilide are produced. Acetanilide furnishes its hydrochloride and diacetylaniline. *p*-Toluidine gives its hydrochloride, aceto-*p*-toluidide, and diaceto-*p*-toluidide, the *hydrochloride* of which has m. p. 120°. α- and β-Naphthylamine yield their hydrochlorides and the acetonaphthalides; aceto-α- and -β-naphthalide *hydrochlorides* have m. p. 137° and 152° respectively. With benzylamine, the chief product of the reaction is acetylbenzylamine hydrochloride, m. p. 134°.

Diethylamine, diamylamine, methylaniline, ethylaniline, and piperidine yield their respective hydrochlorides, together with those of their acetyl derivatives. Acetomethylanilide *hydrochloride* has m. p. 71°.

Tripropylamine gives a mixture of its *hydrochloride*, m. p. 90°, with the acetyl chloride additive *compound*, $N(C_3H_7)_3,CH_3\cdot COCl$. The additive *compound* of dimethylaniline has m. p. 60—70°. Diethylaniline, diethyl-*p*-toluidine, pyridine, quinoline, quinaldine, and acridine also yield additive *compounds* with acetyl chloride. The pyridine additive *compound* has m. p. 71°, and the acridine *compound*, m. p. 236°.

Quinine yields the additive *compound*, $C_{20}H_{24}O_2N_2,2CH_3\cdot COCl$. *m*-Nitroaniline gives a mixture of its hydrochloride with that of its acetyl derivative. E. G.

Action of Iodoform on Organic Bases. WILLIAM M. DEHN and RAY B. CONNER (*J. Amer. Chem. Soc.*, 1912, **34**, 1409—1414).—In earlier papers (Abstr., 1911, i, 829, 914; this vol., i, 240, 242), it has been shown that when certain halogen derivatives of methane and ethane are added to solutions of organic bases in dry ether, molecular compounds are produced. It has now been found that iodoform reacts with organic bases in a similar manner to form compounds containing one mol. of iodoform with one, two, or three mols. of the base. The reactions are much accelerated by direct sunlight. The molecular compounds are readily decomposed by an excess of the base, by water, by heat, and by hot organic solvents. The following compounds are described.

The diethylamine *compound*, $NHEt_2,CHI_3$, m. p. 124°, crystallising in white prisms: the triethylamine *compound*, NEt_3,CHI_3; the dipropylamine *compound*, $NH(C_3H_7)_2,CHI_3$, m. p. 144°; the diamylamine *compound*, $NH(C_5H_{11})_2,CHI_3$, m. p. 221°, forming prismatic needles. *iso*Propylamine, *iso*butylamine, *iso*amylamine, and allylamine yield heavy, brown oils.

The benzylamine *compound*, $2CH_2Ph\cdot NH_2,CHI_3$, m. p. 158°, forms long, yellow prismatic needles. With phenylhydrazine, a molecular compound is not obtained, but phenylhydrazine hydriodide, iodobenzene, and traces of phenylcarbimide are produced. The piperidine *compound*, $C_5H_{11}N,CHI_3$, m. p. 107°, forms white or pale yellow needles, and when distilled with steam yields piperidine hydriodide, iodoform, formic acid, and traces of di-iodoacetylene. The pyridine

compound, $3C_5H_5N,CHI_3$, m. p. 183°, crystallises in white needles, and is decomposed by water with formation of iodoform, iodic acid, and pyridine hydriodide. The *a*-picoline *compound*, $2C_5H_4MeN,CHI_3$, is obtained as a red, gummy mass, and when heated with water yields iodine, iodoform, and picoline hydriodide. Lutidine gives a dark brown oil. Collidine yields a dark brown oil and long, transparent needles. The quinoline *compound*, $2C_9H_7N,CHI_3$, m. p. 132°, forms small, reddish-brown needles. The caffeine *compound*,

$$2C_8H_{10}O_2N_4,CHI_3,$$

has m. p. 154°. The triphenylphosphine *compound*,

$$2P(C_6H_5)_3,CHI_3,$$

m. p. 129°, is an amorphous, yellow substance.

Various other bases yield dark-coloured precipitates, which have not yet been investigated; that furnished by morphine has m. p. 248°. E. G.

Isolation of Betaine Hydrochloride from Molasses Residue. FELIX EHRLICH (*Ber.*, 1912, 45, 2409—2413).—Stoltzenberg's method (this vol., i, 680) of isolating betaine hydrochloride from molasses residue differs only in unessential details from the author's patented process (1904, D.R.-P. 157173). Since betaine hydrochloride is easily purified, is not hydrated or hygroscopic, can be dried at 110°, and is extensively hydrolytically dissociated in aqueous solution, and can be used with the customary indicators, the author proposes that it shall be the standard substance in the preparation of solutions for acidimetry and alkalimetry. C. S.

Isomeric Allylamines. PRAFULLA CHANDRA RÂY and RASIK LAL DATTA (*J. and Proc. Asiatic Soc. Bengal*, 1912. Reprint 1 p.).—Hydrolysis of allylthiocarbimide by dilute sulphuric acid gives a poor yield of allylamine, b. p. 57—58° (Hofmann, *Ber.*, 1867, 1, 182; Rinne, Abstr., 1874, 50). The substitution of 20% hydrochloric acid for sulphuric acid gives a better yield of an allylamine, b. p. 55—58° (Gabriel and Eschenbach, Abstr., 1897, i, 395). On repeating the latter experiment, the authors find that the bulk of the amine has b. p. 53—54°, only a small portion passing over between 57° and 58°. It therefore appears that a third isomeric allylamine is formed during hydrolysis of the thiocarbimide by hydrochloric acid. H. W.

The Action of Hydrogen Peroxide on Hexamethylenetetramine. CONWAY VON GIRSEWALD (*Ber.*, 1912, 45, 2571—2576).—In many reactions, hydrogen peroxide acts as a monobasic acid, dissociating into the ions $H^{\cdot}$ and $O{\cdot}OH'$. In accordance with this behaviour, when hexamethylenetetramine is dissolved in excess of 30% hydrogen peroxide and the solution evaporated in a vacuum, thick, colourless crystals of a salt, *hexamethylenetetramine hydrogen peroxide*, $(CH_2)_6N_4,H_2O_2$, are obtained. It decomposes with explosion under the action of concentrated sulphuric acid, and liberates chlorine from concentrated hydrochloric acid. The solution shows the characteristic properties of the components.

When acids are present, the dissociation of the hydrogen peroxide is

prevented, and it reacts with hexamethylenetetramine forming a peroxide, namely, hexamethylenetriperoxidediamine,

$$N(CH_2\cdot O\cdot O\cdot CH_2)_3N$$

(compare Baeyer and Villiger, Abstr., 1900, i, 626). Citric acid is the most convenient acid to use in the preparation, the reagents being used in the proportion: 28 grams of hexamethylenetetramine, 42 grams of citric acid, and 140 grams of 30% hydrogen peroxide. The compound separates on warming the solution.

Hexamethylenetriperoxidediamine is a dangerously explosive substance, its explosive properties being much greater than those of mercury fulminate. T. S. P.

Preparation of *d*-Glucosamine. CARL NEUBERG (*Biochem. Zeitsch.*, 1912, **43**, 500—507).—This substance can be conveniently prepared by heating the calcium-free lobster-shells with concentrated hydrochloric acid in a water-bath. After evaporating and allowing the crystals to separate from the concentrated solution, alcohol should be added. S. B. S.

Conversion of Aminoethyl Alcohol (Colamine) into Choline. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, **80**, 409—411).—Aminoethyl alcohol has been found in lecithin preparations from a number of sources. The name colamine is suggested for it. When methylated with methyl iodide and methyl-alcoholic potassium hydroxide it is converted into choline. Intermediate products, such as monomethyl- and dimethyl-aminoethyl alcohol are not formed.

It is considered that choline is formed in the plant as a degradation product of methylated lecithin. E. F. A.

Iminotetronic Acid. RICHARD ANSCHÜTZ (*Ber.*, 1912, **45**, 2374—2378).—Ethyl sodiocyanoacetate and acetylglycollyl chloride react in benzene to form *ethyl α-cyano-γ-acetoxyacetoacetate*,

$$OAc\cdot CH_2\cdot C(OH)\!:\!C(CN)\cdot CO_2Et,$$

m. p. 49·5—50·5°, long needles, from which *α-cyanotetronic acid*, $CN\cdot C{<}\begin{matrix}C(OH)\cdot CH_2\\ CO\text{——}O\end{matrix}$, decomp. 173—174°, is obtained, in the form of the potassium salt, by the action of alcoholic potassium ethoxide, and *ethyl iminotetron-α-carboxylate*, $CO_2Et\cdot C{<}\begin{matrix}C(OH)\text{—}CH_2\\ C(\!:\!NH)\cdot O\end{matrix}$, decomp. 243·5°, by boiling with alcohol. The latter, which yields the potassium salt of the former by boiling with alcoholic potassium ethoxide, is shown to be identical with Benary's ester-amide of tetramic acid (Abstr., 1911, i, 672). C. S.

The Walden Rearrangement. VIII. Conversions of *d*-Glutamic Acid. EMIL FISCHER and ANNIBALE MORESCHI (*Ber.*, 1912, **45**, 2447—2453).—Natural *d*-glutamic acid is converted by nitrous acid into *l*-α-hydroxyglutaric acid. Nitrosyl chloride or hydrogen chloride and nitrous acid transform it into *l*-α-chloroglutaric acid, which, however, yields *d*-α-hydroxyglutaric acid. The last trans-

formation is effected either by boiling with water or by cold dilute sodium hydroxide, or by silver oxide and water at the ordinary temperature. In all three cases the hydroxy-acid obtained has the same rotatory power: this is contrary to observations in similar cases, especially that of chlorosuccinic acid.

The *sodium* salt of *l*-α-hydroxyglutaric acid forms a colourless, granular powder, $[\alpha]_D^{19}$ $-8{\cdot}65°$. The free acid has a very small lævorotation.

l-α-Chloroglutaric acid has m. p. 99° (corr.), $[\alpha]_D^{18}$ $-12{\cdot}5°$. It is converted into *d*-α-hydroxyglutaric acid, $[\alpha]_D^{25}$ $+8{\cdot}58°$, without any racemisation. E. F. A.

Preparation of Derivatives of Glycollic Carbamides. ARNOLD VOSWINKEL (D.R.-P. 247270).—When bromoacetylcarbamide, $NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_2Br$ (9·5 parts), is boiled for twelve hours with an alcoholic solution of anhydrous sodium acetate (4·1 parts), it furnishes *carbomethoxyacetylcarbamide*,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}CH_3,$$

long, spear-like crystals, m. p. 177°; the following analogous *compounds* were also obtained; from bromoacetylcarbamide with sodium *iso*valerate, m. p. 165°; with sodium bromo*iso*valerate, glistening, mother-of-pearl scales, m. p. 160°; with sodium benzoate, m. p. 200°, and with sodium salicylate, m. p. 235°; these compounds are of therapeutic value. F. M. G. M.

Erysolin, a Thiocarbimidosulphone from Erysimum perowskianum. WILHELM SCHNEIDER and HANS KAUFMANN (*Annalen*, 1912, **392**, 1—15).—The seeds of *Erysimum perowskianum* contain a substance, probably a glucoside, from which a crystalline thiocarbimidosulphone, closely related to cheirolin (Abstr., 1910, i, 658), has been obtained, in 0·05% yield, calculated on the weight of the fresh seeds. The sulphone, which is called *erysolin*, is isolated in almost the same manner as cheirolin from wallflower seeds (*loc. cit.*).

Erysolin, $C_6H_{11}O_2NS_2$, m. p. 59—60°, colourless prisms, is optically inactive. It reacts with alcoholic ammonia to form a *thiocarbamide*, $C_6H_{14}O_2N_2S_2$, m. p. 143—144°, and is hydrolysed by boiling *N*-hydrochloric acid, yielding hydrogen sulphide, carbon dioxide, and a *base*, $C_5H_{13}O_2NS$ (*hydrochloride*, m. p. 160°, colourless leaflets; *platinichloride*, decomp. 205–207°), the oxidation of which by nitric acid, D 1·5, at 200° yields methanesulphonic acid. A fuller examination of the natural erysolin has not been undertaken on account of lack of material, but the preceding facts, considered in conjunction with the close relation of erysolin to cheirolin, leave little doubt that erysolin is *methyl-δ-thiocarbimidobutylsulphone*, $CH_3{\cdot}SO_2{\cdot}[CH_2]_4{\cdot}NCS$. This supposition has been verified by the synthesis of the latter. *Methyl γ-cyanopropyl sulphide*, $CN{\cdot}[CH_2]_3{\cdot}SMe$, b. p. 218°, obtained from γ-chlorobutyronitrile and alcoholic sodium methylmercaptide at 0°, is reduced by sodium and boiling alcohol to *methyl δ-aminobutyl sulphide*, $NH_2{\cdot}[CH_2]_4{\cdot}SMe$, b. p. 188—190°. This base, which has an odour resembling that of piperidine, forms a *hydrochloride*, m. p. 153—154°, leaflets, *oxalate*, decomp. 202°, *picrate*, m. p. 116—118°, yellow needles,

picrolonate, decomp. 172—174°, canary yellow plates, *thiocarbamide*, m. p. 42—45°, and NS-*dimethiodide*, $C_9H_{23}NSI_2$, m. p. 142°, which is very stable. (The last fact is interesting in connexion with the non-existence of *NS*-dimethiodides of $RS{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ [this vol., i, 191] and the instability of the *NS*-dimethiodide of $CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ [Schneider, *loc. cit.*]).

Methyl δ-aminobutyl sulphide in acetone is oxidised by concentrated hydrogen peroxide to *methyl-δ-aminobutylsulphoxide*, $NH_2{\cdot}[CH_2]_4{\cdot}SOMe$, which forms an *oxalate*, m. p. 174—179°, *picrate*, m. p. 149°, and *picrolonate*, m. p. 195° (decomp.). Methyl δ-aminobutyl sulphide hydrochloride is oxidised by aqueous potassium permanganate to the *sulphone*, $NH_2{\cdot}[CH_2]_4{\cdot}SO_2Me$, m. p. 42°, b. p. 165°/4 mm., which is identical with the base obtained by the hydrolysis of erysolin. It forms a hydrochloride, m. p. 160°, platinichloride, decomp. 205—207°, *aurichloride*, m. p. 187—189°, yellow plates, *picrate*, decomp. 216°, *picrolonate*, m. p. 144°, decomp. 205°, yellow needles, *thiocarbamide*, m. p. 147°, and *dimethiodide*, $C_8H_{20}O_2NSI$, m. p. 138°, colourless needles.

By Braun's method (this vol., i, 693), the sulphone is converted into methyl-δ-thiocarbimidobutylsulphone, which proves to be identical with erysolin.

C. S.

Fulminic Acid. VI. Polymeric Fulminic Acids. HEINRICH WIELAND and ARTUR BAUMANN (*Annalen*, 1912, **392**, 196—213).—Of the three polymerides, $C_3H_3O_3N_3$, of fulminic acid, only the constitution of *iso*cyanilic acid remains to be determined; meta-fulminuric acid is 4 : 5-dioximino-4 : 5-dihydro*iso*oxazole (Abstr., 1909, i, 369), and *iso*fulminuric acid is 3-hydroxyfurazan-4-carbonamide, as suggested by Nef, who obtained the substance by the action of ammonia on chloroformoxime. The authors have now thoroughly examined this reaction. A cold ethereal solution of chloroformoxime (obtained from silver fulminate and hydrochloric acid) is treated with *N*-ammonia. *iso*Fulminuric acid is not a direct product of the reaction. Doubtless fulminic acid is formed and immediately polymerises to meta-fulminuric acid. From this, by the action of the ammonia, the intermediate products of the reaction are obtained. These products are 3-hydroxyfurazan-4-carbonamidine, oximinomalonamideamidoxime, oximinomalonohydroxamamidine (these three are the solid products of the reaction; the first two are the main products, and yield *iso*fulminuric acid by warming with ammonia), a yellow oil, and 3-amino-4-oximino-*iso*oxazolone (Abstr., 1909, i, 610). The separation of these substances is described.

The *amidoxime* of *oximinomalonamide*,

$$NOH{:}C(NH_2){\cdot}C({:}NOH){\cdot}CO{\cdot}NH_2,$$

decomp. 170°, sulphur-yellow needles, forms colourless solutions in acids and yellow solutions in alkalis, and reacts with sodium nitrite in cold 15% hydrochloric acid to form nitrous oxide and a *substance*, $C_3H_5O_3N_3$, m. p. 215° (decomp.), colourless needles, which is isomeric, but not identical, with oximinomalonamide, $\begin{matrix}NH\\ |\\ O\end{matrix}\!\!>\!C(CO{\cdot}NH_2)_2$. This

substance is hydrolysed by boiling concentrated barium hydroxide, yielding oximinomalonic acid and *oximinomalonamic acid*,

$$\mathrm{CO_2H \cdot C({:}NOH) \cdot CO \cdot NH_2},$$

m. p. 137° (decomp.).

The *amidine* of *oximinomalonhydroxamic acid*,

$$\mathrm{NOH{:}C(OH) \cdot C(NOH) \cdot C({:}NH) \cdot NH_2},$$

m. p. 177° (decomp.), colourless needles, is produced only in small quantity by the interaction of ammonia and chloroformoxime; together with the amidoxime, it is more conveniently obtained by allowing oximinocyanoacethydroxamic acid and an excess of aqueous ammonia to evaporate in the air. The amidine forms colourless solutions in acids and yellow solutions in alkalis, develops a bluish-violet coloration with dilute ferric chloride, forms an intensely yellow *silver* salt, and reacts with nitrous acid to form *oximinomalonamidine*,

$$\mathrm{CO_2H \cdot C({:}NOH) \cdot C({:}NH) \cdot NH_2},$$

decomp. 283°, colourless needles, which does not give a coloration with ferric chloride, but develops a deep violet coloration with ferrous sulphate and sodium acetate.

*iso*Fulminuric acid is best obtained by boiling the two products mentioned above with an excess of aqueous ammonia for three hours, and decomposing the resulting ammonium *iso*fulminurate by hydrochloric acid. It has m. p. 202° (decomp.), and is much less soluble in water or alcohol than Ehrenberg states. Reactions of the acid with metallic salts and so forth are mentioned. By hydrolysis with boiling barium hydroxide, it yields barium 3-hydroxyfurazan-4-carboxylate. *iso*-Fulminuric acid is also obtained from metafulminuric acid, either by its spontaneous decomposition in a sealed vessel (Scholvien's β-*iso*-fulminuric acid, m. p. 196°, stated to be so produced, is ordinary *iso*-fulminuric acid), or by heating it with a slight excess of sodium carbonate on the water-bath for a few minutes.

5-*Imino*-4-*oximino*-3-*hydroxy*-4:5-*dihydro*iso*oxazole*,

$$\mathrm{NOH{:}C}\!<\!\begin{matrix}\mathrm{C({:}NH) \cdot O} \\ \mathrm{C(OH){:}N}\end{matrix},$$

decomp. 143°, orange-yellow, crystalline powder, is obtained by warming metafulminuric acid for two to three minutes with *N*-sodium carbonate at 60—70°, cooling to 0°, and faintly acidifying with hydrochloric acid. It is unstable, gives no coloration with ferric chloride, and is converted into oximinomalonhydroxamic acid by keeping with dilute hydrochloric acid. C. S.

Mercury Fulminate. Robert Philip (*Zeitsch. ges. Schiess- und. Sprengstoffwesen*, 1912, 7, 109—112, 156—162, 180—182, 198—200, 221—225).—A series of papers dealing with different methods of preparing mercury fulminate, its purification, and analysis, with the theoretical considerations involved in these operations. F. M. G. M.

Nitroglyoxime. Eugen Bamberger and Umetaro Suzuki (*Ber.*, 1912, 45, 2740—2758).—The preparation and properties of nitroglyoxime have been investigated.

Nitroglyoxime is obtained in good yield by the regulated action of nitric acid (D 1·4—1·41) on glyoxime dissolved in a mixture of ether

and water. The presence of small quantities of nitrous acid appears essential to the success of the operation. It appears probable that the first stage of the reaction consists in the formation of nitrosoglyoxime, which is subsequently oxidised to nitroglyoxime, the nitrous acid simultaneously formed then acting on a further quantity of the original material:

$$\begin{array}{l} H\cdot C{:}N\cdot OH \\ H\cdot C{:}N\cdot OH \end{array} \xrightarrow{HNO_2} \begin{array}{l} ON\cdot C{:}N\cdot OH \\ H\cdot C{:}N\cdot OH \end{array} \xrightarrow{HNO_3} \begin{array}{l} O_2N\cdot C{:}N\cdot OH \\ H\cdot C{:}N\cdot OH \end{array}.$$

Nitroglyoxime crystallises in white, silky needles, which swell up at 111°. The temperature is, however, largely dependent on external circumstances, such as rate of heating, width of capillary tube, etc. On further heating, a second more violent swelling occurs accompanied by evolution of gas. In the pure state it is stable. In aqueous solution, it gives a red coloration with ferric chloride, which, on keeping, increases in intensity and does not pass into ether when agitated with the latter. It yields a scarlet *ammonium* salt, a *potassium* salt, $C_2H_2O_4N_3K$, terra-cotta needles, a *silver* salt,

$$C_2H_2O_4N_3Ag,H_2O,$$

and a *copper* salt, $(C_2H_2O_4N_3)_2Cu,2H_2O$, dark green, almost black needles. The water of crystallisation in the two latter salts could not be directly determined, since they decompose in a vacuum at 50—60°. The *lead* salt, $(C_2H_2O_4N_3)Pb\cdot O\cdot Pb(C_2H_2O_4N_3)$, is formed as a yellow precipitate when aqueous solutions of lead acetate and nitroglyoxime are mixed, and is adapted for the detection of small quantities of the latter, since its aqueous suspension, when boiled, becomes colourless and almost clear.

The *hydrazine* salt, $C_2H_2O_4N_3(NH_3\cdot NH_2)$, decomposing on rapid heating at 95°, when treated with acetone deposits white *needles*, decomposing at about 92°, according to the method of heating.

Dibenzoylnitroglyoxime, white needles decomposing at 151·5°, is obtained by the action of benzoyl chloride and potassium hydroxide on an aqueous solution of nitroglyoxime.

When a solution of nitroglyoxime in water is slowly distilled, decomposition occurs with the formation of nitrous oxide, nitrogen, nitric oxide, carbon dioxide, hydrocyanic acid, formic acid, oxalic acid, hydroxylamine, and ammonia, together with an oily acid *substance*, which has a powerful aldehydic odour. It is soluble in sodium hydroxide, but apparently unable to react with phenylhydrazine or *p*-nitrophenylhydrazine. It does not reduce ammoniacal silver nitrate or Fehling's solution. When allowed to remain in contact with water, it deposits a white *substance*, m. p. about 105°.

[With Jul. Potschiwauscheg.]—Methazonic acid (Meister, Abstr., 1907, i, 885; Steinkopf, Abstr., 1909, i, 559) is transformed into nitroglyoxime when sulphuric acid is slowly added to a solution of the potassium salt and sodium nitrite at 0—4°.

[With Marie Finkelstein.]—Ulpiani's compound,

$$2C_2H_3O_3N_3,H_2O,$$

prepared from glyoxime and nitrogen peroxide, proves to be a mixture of glyoxime and nitroglyoxime with small quantities of a third substance. H. W.

Reduction of Ethyl Diazoacetate. II. AUGUST DARAPSKY and MORESHWAR PRABHAKAR (*Ber.*, 1912, **45**, 2617—2625. Compare this vol., i, 543).—Hydrazinoacetic acid is obtained in good yield (65%) by reducing *iso*nitroaminoacetic (nitrosohydroxylaminoacetic) acid,

$$OH\cdot N(NO)\cdot CH_2\cdot CO_2H,$$

with sodium amalgam in alkaline solution (compare Traube and Hoffa, Abstr., 1897, i, 138; 1898, i, 235).

Ethyl nitrosohydrazinoacetate, which was previously described as an oil, has now been obtained in long, stout, colourless prisms, m. p. 33°. By reducing ethyl diazoacetate with zinc dust and acetic acid in ethereal solution, Curtius and Jay (Abstr., 1889, 340) obtained a hydrazine compound, presumably the acetate of ethyl hydrazinoacetate. The authors have repeated the reduction, but from the product, only ethyl aminoacetate could be isolated.

Diazoacetic acid is readily reduced by zinc dust and sodium hydroxide to hydrazinoacetic acid, which is also obtained in good yield by reducing Pechmann's (Abstr., 1895, i, 642) ethyl sulphohydrazimethylenecarboxylate with sodium amalgam in aqueous solution. The latter reaction is best interpreted on the assumption that the sulpho-compound has the structure $SO_3K\cdot NH\cdot N\colon CH\cdot CO_2Et$, and not the cyclic structure, $\begin{matrix} NH- \\ | \\ SO_3K\cdot N- \end{matrix}\!\!>CH\cdot CO_2Et$, proposed by Pechmann.

Attempts to prepare the hydrazino-acid by reducing the hydrazone of glyoxylic acid proved fruitless. The semicarbazone, on the other hand, is readily reduced to $NH_2\cdot CO\cdot NH\cdot NH\cdot CH_2\cdot CO_2H$, which, however, was not isolated, but hydrolysed by hydrochloric acid to hydrazinoacetic acid. F. B.

Estimation of Active Hydrogen in Organic Compounds by Magnesium Methyl Iodide. TH. ZEREWITINOFF (*Ber.*, 1912, **45**, 2384—2389).—In contrast to the results obtained by Hibbert (Trans., 1912, **101**, 328), the author finds that methyl, ethyl, and propyl alcohols yield practically the theoretical amount of methane by interaction with magnesium methyl iodide in pyridine.

From the results of experiments on the reaction between magnesium methyl iodide and ethylenediamine, *o*-, *m*-, and *p*-phenylenediamines, benzidine, *o*-tolidine, *oo'*-diaminostilbene, and 1:2-naphthylenediamine in pyridine or anisole, it is found that compounds containing two amino-groups yield two molecules of methane at the ordinary temperature and three molecules by warming; the fourth aminic hydrogen atom cannot be made to react with magnesium methyl iodide (compare Abstr., 1908, i, 593). The abnormal behaviour of malonamide (*loc. cit.*), which by warming reacts with 4 molecules of magnesium methyl iodide, is due to the activity of one of the methylene hydrogen atoms.

Indene, fluorene, and $\alpha\alpha'$-dinaphthafluorene do not react with magnesium methyl iodide in pyridine at the ordinary temperature; however, by warming to 85°, one molecule of methane is evolved. Phenylfluorene and α-naphthyldinaphthafluorene also only react when warmed. Phenylfluorenol and α-naphthyldinaphthafluorenol partly react with magnesium methyl iodide at the ordinary temperature, but

must be heated to 85° in order that one molecule of methane may be liberated.

Only hydrocarbons of the fluorene type react with magnesium methyl iodide; diphenylmethane, triphenylmethane, dinaphthylmethane, and trinaphthylmethane (α and β) do not react either in the cold or by warming. C. S.

Polymerisation of *cyclo*Pentadiene. HANS STOBBE and FRITZ REUSS (*Annalen*, 1912, **391**, 151—168).—By the spontaneous polymerisation of *cyclo*pentadiene, *bicyclo*pentadiene is the only product at temperatures up to 100°; at higher temperatures, for example, at 135°, *polycyclo*pentadiene is also formed.

In darkness at 20°, the polymerisation to the bicyclic compound is practically complete in thirty days, proceeding rapidly in the early stages and then more slowly as the process approaches completion. The rate of polymerisation is affected only very slightly by air or light. The course of the polymerisation is estimated by the change in the refractive index.

*cyclo*Pentadiene is prepared by the distillation of commercial di*cyclo*pentadiene at 166—167°, the fraction, b. p. 41·5—42°, being redistilled until its refractive indices, n_C^{20} 1·44113 and n_F^{20} 1·45380, are constant. Di*cyclo*pentadiene, m. p. 32°, b. p. 70°/24 mm., is obtained by the spontaneous polymerisation of *cyclo*pentadiene, and has n_C^{20} 1·51047 and n_F^{20} 1·52181. C. S.

$\Delta^{1:3}$-*cyclo*Hexadiene. CARL D. HARRIES (*Ber.*, 1912, **45**, 2586. Compare this vol., i, 343).—The hydrocarbon combines with bromine (one mol.) in chloroform solution, yielding the dibromide, m. p. 108°, described by Crossley (Trans., 1904, **85**, 1403). F. B.

The Problem of Benzene Structure Reviewed from Thermochemical Standpoint. WILLEBRORD TOMBROCK (*Chem. News*, 1912, **106**, 155—156).—The heat liberated in the successive stages of the hydration of benzene is less than that set free in similar changes in open-chain compounds, and by ascribing the differences involved to the absorption of energy in the benzene ring, it is shown that information may be obtained in reference to the benzene structure. By assuming Kekulé's formula and correcting the heat of hydration for the influence of the ring structure, a value is obtained which agrees closely with the heat of hydration of open-chain compounds. When the centric formula is assumed, this concordance is no longer found.

H. M. D.

Preparation of Nitrostyrene and of Arylnitroethanol Derivatives. KARL W. ROSENMUND (D.R.-P. 247817. Compare Abstr., 1905, i, 65; 1911, i, 34).—Pseudo-acids of the general formula

X·CH(OH)·CH:NO·OMe (X = aryl)

are readily obtained by the action of nitromethane on acylated hydroxyaryl aldehydes; these substances by treatment with acids furnish derivatives of nitrostyrene, which by subsequent hydrolysis with alkalis yield the corresponding hydroxy-compounds.

Ethylcarbonatobenzaldehyde, m. p. 18°, b. p. 175—180°/in a vacuum, when treated with nitromethane in sodium methoxide solution furnishes *ethylcarbonatonitrostyrene*, $OEt{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}NO_2$, yellow needles, m. p. 110°, and *ethylcarbonatophenylnitroethanol* $C_2H_5O{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$, yellow needles, m. p. 91·5°, whilst benzoylvanillin yields *vanillylnitroethylene*,

$$OH{\cdot}C_6H_3(OMe){\cdot}CH{:}CH{\cdot}NO_2,$$

intensely yellow needles, m. p. 161°, and *vanillylnitroethanol*,

$$OH{\cdot}C_6H_3(OMe){\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2,$$

a yellow oil.

Dibenzoylprotocatechualdehyde, m. p. 96—97°, yields *dibenzoyldioxynitrostyrene*, $C_6H_3(OBz)_2{\cdot}CH{:}CH{\cdot}NO_2$, yellow needles, m. p. 143—144°, which when treated with alcoholic alkaline hydroxides furnishes *nitrodihydroxystyrene*, $C_6H_3(OH)_2{\cdot}CH{:}CH{\cdot}NO_2$, yellow needles, m. p. 155° (decomp.). F. M. G. M.

Phenanthrene-10-sulphonic Acid and Certain of its Derivatives. HÅKAN SANDQVIST (*Annalen*, 1912, **392**, 76—91).—*Phenanthrene*-10-*sulphonic acid*, $C_{14}H_9{\cdot}SO_3H,2H_2O$, m. p. 134° (decomp.) (174° when anhydrous), leaflets or needles, is obtained in the form of the sodium salt in about 60% yield by the interaction of aqueous sodium sulphite and 10-bromophenanthrene at 330—340° for nine hours; the method is not satisfactory on the small scale. A process is described whereby the acid is obtained by the prolonged action of concentrated sulphuric acid on finely divided phenanthrene at the ordinary temperature. The molecular conductivities at 18° of the acid in aqueous solution, $v = 34{\cdot}25$, 63·69, 127·8, 511·5, and 1019, are 319·4, 324·7, 329·2, 334·7, and 334·7 respectively.

The salts, obtained from the acid in aqueous solution and the hydroxide, oxide, or carbonate of the requisite metal, crystallise more readily and are much more soluble than most of the salts of other phenanthrenesulphonic acids. The following are described, the numbers in brackets denoting the weight of anhydrous salt which will dissolve in 100 grams of water at 20°: *potassium* salt, leaflets containing H_2O (0·84); *ammonium* salt, needles or leaflets containing $1\frac{1}{2}H_2O$ (4·41); *sodium* salt, leaflets containing $2H_2O$ (1·63); *calcium* salt, leaflets with $2H_2O$ (0·30); *barium* salt, leaflets with $3H_2O$ (0·13); *magnesium* salt, leaflets with $5H_2O$ (0·22); *zinc* salt, leaflets and plates with $6H_2O$ (0·15); *ferrous* salt, almost white leaflets with $6H_2O$ (0·16); *lead* salt, needles or leaflets with $4H_2O$; *copper* salt, green plates with $4H_2O$ (0·26); *silver* salt, anhydrous leaflets (0·52).

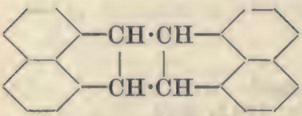
Phenanthrene-10-sulphonyl chloride, which is hydrolysed completely by water at 230°, is converted in benzene solution by concentrated aqueous ammonia into the *sulphonamide*, m. p. 193·5°, needles. *Methyl phenanthrene*-10-*sulphonate*, m. p. 106°, and the *ethyl* ester, m. p. 108°, are obtained from the potassium salt and the alkyl sulphate.

When heated at 250—260°, anhydrous ammonium phenanthrene-10-sulphonate is partly converted into ammonium phenanthrene-2-sulphonate and partly changed to phenanthrene and an ammonium phenanthrenedisulphonate.

Sodium phenanthrene-10-sulphonate yields phenanthraquinone by

oxidation with boiling chromic and acetic acids, but scarcely any quinone is formed when one part or more of potassium phenanthrene-3-sulphonate is present. C. S.

Photochemical Changes of Acenaphthylene. I. KARL DZIEWOŃSKI and G. RAPALSKI [and, in part, Z. LEYKO] (*Ber.*, 1912, **45**, 2491—2495*).—On exposure of yellow acenaphthylene in benzene solution to sunlight, it undergoes polymerisation, the new compound crystallising in slender, colourless needles of silky lustre, m. p. 306—307°; this is completely saturated, and does not dissolve in concentrated sulphuric acid. It has the composition $(C_{12}H_8)_2$, and, when oxidised with chromic acid, is converted almost quantitatively into naphthalic anhydride. This behaviour characterises it as *dinaphthylenecyclobutane* (annexed formula). In view of the seven rings present, the name *heptacyclene* is proposed.



In addition to the above an isomeric hydrocarbon crystallising in well formed, large, monoclinic prisms, m. p. 234°, is also formed. E. F. A.

Fluoroanilines and Fluorophenols. I. J. RINKES (*Chem. Weekblad*, 1912, **9**, 778—783).—A number of fluoro-derivatives of aniline and phenol have been prepared. *p*-Fluoroaniline is obtained by reducing *p*-fluoronitrobenzene with iron-powder and sulphuric acid, (compare Wallach and Heusler, Abstr., 1888, 362). It forms colourless crystals, m. p. −1·9°, b. p. 85°/19 mm. The *hydrochloride*, formed by the action of hydrogen chloride on the base in solution in carbon tetrachloride, has b. p. 167°/27 mm.

Diazotisation of *p*-fluoroaniline by Gattermann's method yields p-*fluorophenol*, white crystals, m. p. 46·0°, b. p. 81·5°/13 mm.

o-*Fluoroaniline* is prepared by reduction of *o*-fluoronitrobenzene with iron and very dilute sulphuric acid. Repeated distillation yields a product, m. p. −34·6°, b. p. 68·5°/14 mm. It is colourless, and has a faint aniline-like odour. On diazotisation, it resinifies, so that the corresponding phenol could not be prepared. A. J. W.

Action of Formaldehyde on β-Phenylethylamine. HERMAN DECKER and PAUL BECKER (*Ber.*, 1912, **45**, 2404—2409).—A boiling alcoholic solution of β-phenylethylamine (*platinichloride*, m. p. 253—254°, yellow leaflets) reacts with methyl sulphate in the presence of sufficient sodium carbonate to keep the solution neutral, to form *β-phenylethyltrimethylammonium iodide*, $CH_2Ph\cdot CH_2\cdot NMe_3I$, m. p. 227—230°, colourless leaflets; the corresponding *platinichloride* has m. p. 250°. β-Phenylethylamine hydrochloride and an excess of 40% formaldehyde at 130—140° for three hours yield the *hydrochloride*, white leaflets, of *β-phenylethyldimethylamine*, $CH_2Ph\cdot CH_2\cdot NMe_2$, b. p. 204—206°, which forms a *picrate*, m. p. 133—134°, yellow needles, and *platinichloride*, m. p. 206—208° (corr.), and yields the preceding quaternary ammonium iodide by methylation as above.

The base obtained by the decomposition of β-phenylethylglycine or its hydrochloride at their m. p.'s (Abstr., 1911, i, 714) is *β-phenylethyl-*

* and *Bull. Acad. Sci. Cracow*, 1912, *A*, 714—720.

methylamine, $CH_2Ph\cdot CH_2\cdot NHMe$. This base, which forms a *hydrochloride* and *platinichloride*, m. p. 154—156° and 225—226° respectively, reacts with formaldehyde as above, to form β-phenylethyldimethylamine. C. S.

Syntheses in the Fatty Aromatic Series. VIII. Phenol Bases. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1912, **45**, 2504—2522).—Compounds of the type of hordenine,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2,$$

have been prepared, in which by the introduction of additional CH_2 group the NMe_2 is further removed from the benzene ring, in order to examine their pharmacological properties.

γ-o-*Hydroxyphenylpropyldimethylamine* and the isomeric γ-p-*hydroxyphenylpropyldimethylamine*, $OH\cdot C_6H_4\cdot [CH_2]_3\cdot NMe_2$, also δ-p-*hydroxyphenylbutyldimethylamine*, $OH\cdot C_6H_4\cdot [CH_2]_4\cdot NMe_2$, and ε-p-*hydroxyphenylamyldimethylamine*, $OH\cdot C_6H_4\cdot [CH_2]_5\cdot NMe_2$, have been prepared by methods analogous to those used by Barger (Trans., 1909, **95**, 1123) in synthesising hordenine. The phenylalkyl chlorides,

$$Ph\cdot [CH_2]_xCl,$$

were cautiously nitrated, the nitrochloro-compounds,

$$NO_2\cdot C_6H_4\cdot [CH_2]_xCl,$$

acted on by dimethylamine, the nitro-bases,

$$NO_2\cdot C_6H_4\cdot [CH_2]_x\cdot NMe_2,$$

reduced, and the amino-group in the diamines,

$$NH_2\cdot C_6H_4\cdot [CH_2]_x\cdot NMe_2,$$

replaced by hydroxyl. Only in the propyl series is proof given that nitration takes place in the para-position. All four compounds act in the opposite manner to hordenine, since they lower the blood pressure; the effect of *o*-hydroxyphenylpropyldimethylamine is very small.

γ-o-*Hydroxyphenylpropyldimethylamine* is a viscid, almost odourless, faintly yellow-coloured oil. The *hydrochloride* is colourless, m. p. 155—156°; the *platinichloride* forms small, yellow crystals, m. p. 160° (decomp.); the *methiodide* is colourless, m. p. 175°; the *picrate* separates in dark red, stout crystals, m. p. 127°. The *benzoyl* derivative is oily.

γ-p-*Nitrophenylpropyl chloride*, prepared by nitration of γ-phenylpropyl chloride, has b. p. 176—180°. On reduction with tin and hydrochloric acid, p-γ-*chloropropylaniline*, $NH_2\cdot C_6H_4\cdot [CH_2]_3Cl$, is obtained. In addition chlorine enters the benzene ring, but this compound has not been isolated. The aniline is a brown oil with an odour of camphor; the *hydrochloride* has m. p. 174°; the *platinichloride* forms a yellow mass, m. p. 166°, which is decomposed even by cold water; the *benzoyl* derivative has m. p. 118°; the *phenylthiocarbamide* forms slender, colourless crystals, m. p. 125—126°.

The *phenylthiocarbamide* of tetrahydroquinoline, produced from the *o*-isomeride of the above, has m. p. 109°. The behaviour of *p*-chloropropylaniline on distillation and towards potassium hydroxide, carbonate or acetate establishes the absence of any *o*-chloropropylaniline from this product.

γ-p-*Hydroxyphenylpropyl chloride* is a faintly yellow-coloured liquid

b. p. 151—153°/8 mm. The *urethane*, $NHPh\cdot CO\cdot O\cdot C_6H_4\cdot[CH_2]_3Cl$, forms a mass of crystalline threads, m. p. 124°.

γ-p-*Hydroxyphenylpropyl alcohol* (*homotyrosol*), $OH\cdot C_6H_4\cdot[CH_2]_3\cdot OH$, forms colourless crystals resembling snow crystals, m. p. 55°; it gives an indigo-blue coloration with ferric chloride. It tastes only faintly bitter, and is without action on Fehling's solution. It is physiologically indifferent. The *dibenzoyl* derivative crystallises in colourless platelets, m. p. 72°.

γ-p-*Nitrophenylpropyldimethylamine* has b. p. 168—170°/12 mm., 188—191°/22 mm., entirely without decomposition; it is yellow oil, non-miscible with water with a faintly basic odour. The *picrate* is sparingly soluble in alcohol; the *methiodide* separates in small, yellow crystals.

γ-p-*Aminophenylpropyldimethylamine* is a colourless, mobile liquid of strong basic odour, b. p. 150—155°/10 mm., 155—160°/12 mm., with some decomposition. The benzoyl derivative and picrate are oily; the crystalline *hydrochloride* reddens on exposure, and blackens above 200° when heated. The *platinichloride* yields well-formed, yellow crystals, m. p. 201°.

Homohordenine separates in stunted, colourless crystals, m. p. 105—106°. The *picrate* crystallises in lustrous platelets, m. p. 164°; the *hydrochloride* forms plates, m. p. 142°; the *platinichloride* yields red platelets, m. p. 160°; the *methiodide* has m. p. 158°. The lethal dose of homohordenine for rabbits is 0·25 gram.

δ-p-*Nitrophenylbutyl chloride* is a yellow liquid of aromatic odour, b. p. 182—190°/7 mm.

δ-p-*Nitrophenylbutyldimethylamine* is a viscid, odourless oil, b. p. 166—168°/7 mm.; the picrate has m. p. 90—95°.

δ-p-*Aminophenylbutyldimethylamine* has b. p. 154—157°/7 mm., solidifying to a crystalline mass, m. p. 53°; the *picrate* has m. p. 120°; the *hydrochloride* blackens at 215°, m. p. 221°; the *platinichloride* blackens at 210°, m. p. 212°.

δ-p-*Hydroxyphenylbutyldimethylamine* separates in lustrous, colourless crystals, m. p. 97°; the *hydrochloride* has m. p. 154°; other derivatives analysed are the *picrate*, m. p. 124—125°, the *platinichloride*, m. p. 152°, and the *methiodide*, m. p. 214°. The lethal dose of the hydroxyphenylbutyldimethylamine is 0·01 gram.

ε-p-*Nitrophenylamyl chloride* is a pale yellow liquid, b. p. 190—195°/8 mm., with a pleasant sweet odour.

ε-p-*Nitrophenylamyldimethylamine* has b. p. 190—192°/12 mm., and forms a *picrate*, m. p. 185°.

ε-p-*Aminophenylamyldimethylamine* is a viscid liquid of a strongly basic odour, b. p. 179—185°/13 mm.

ε-p-*Hydroxylphenylamyldimethylamine* crystallises in colourless, lustrous needles, m. p. 99°. The *hydrochloride* is oily; the *platinichloride* has m. p. 122°. The lethal dose of a slightly impure preparation was 0·02 gram.

E. F. A.

Acetals Derived from Cyclic Alcohols. MARCEL MURAT and CATHALA (*J. Pharm. Chim.*, 1912, [vii], 6, 289—292).—The condensa-

tion products of formaldehyde with *cyclo*hexanol and the three methyl-*cyclo*hexanols are described.

When hydrogen chloride is passed into *cyclo*hexanol, dissolved in 40% formaldehyde solution, the product $C_6H_{11}O\cdot CH_2\cdot O\cdot C_6H_{11}$, b. p. 279—280°/760 mm., D_0^{24} 0·9716, n_D 1·470, is formed. It is a colourless liquid having a fruity odour and darkening on exposure to light with the liberation of some formaldehyde. It dissolves in sulphuric acid with a blood-red colour, forms substitution products with bromine, and is violently attacked by a mixture of sulphuric and nitric acids, producing adipic acid. When passed over thoria at 400°, it gives rise to hydrogen, ethylene, water, benzene, *cyclo*hexene, and *cyclo*hexanone.

2-Methyl*cyclo*hexanol gives a similar *product*, b. p. 298°/760 mm. (corr.), D_0^{24} 0·9627, n_D 1·477, which with sulphuric and nitric acids yields chiefly *n*-pimelic acid, $CO_2H\cdot[CH_2]_5\cdot CO_2H$. The corresponding *substance* from 3-methyl*cyclo*hexanol has b. p. 301—303° (corr.), D_0^{24} 0·9612, n_D^t 1·470, whilst *that* from 4-methyl*cyclo*hexanol has b. p. 301—303° (corr.), D_0^{24} 0·968, n_D 1·473, and with sulphuric and nitric acids yields β-methyladipic acid. T. A. H.

Behaviour of Phenols, Naphthols, and Phenolcarboxylic Acids Towards Quadrivalent Titanium. OTTO HAUSER and A. LEWITE (*Ber.*, 1912, 45, 2480—2484).—Concentrated solutions of titanium oxide in cold fuming hydrochloric acid or strong sulphuric acid give an intense bluish-red coloration on heating with hydroxy-phenols, for example, phenol, the cresols, thymol, quinol, guaiacol, resorcinol, orcinol, α- and β-naphthol, etc. The reaction is a general one for the detection of hydroxy-groups. Catechol and pyrogallol give a yellow or deep red coloration with dilute solutions of the titanium salt. The two dihydroxynaphthalenedisulphonic acids show violet with the solution of titanium in strong sulphuric acid, but red with a dilute solution.

Halogen and nitrogen derivatives of the phenols do not show the reaction; the colour is not influenced by other organic substituents so long as the hydroxy-group remains intact.

Well characterised compounds of titanium with phenols or naphthols could not be obtained. More favourable results are given by the phenolcarboxylic acids, which give a yellow coloration with titanic acid.

Salicylic acid thus gives an intense reddish-yellow coloration in alcoholic solution; on evaporation, red flakes separate. On boiling and dilution with water, an amorphous, yellow precipitate is obtained. Probably the solution contains a complex, titanisalicylic acid, and the precipitates represent hydrolytic decomposition products.

By mixing a concentrated solution of titanic acid in cold fuming hydrochloric acid with an excess of salicylic acid and adding in small portions 5% ammonium solution, while the whole is warmed and stirred until the solution is only just acid, the *ammonium* salt of a *dititanisalicylic acid*, $O{:}[Ti(O\cdot C_6H_4\cdot CO_2\cdot NH_4)(O\cdot C_6H_4\cdot CO_2H)_2]_2$, is obtained in yellowish-red, prismatic crystals.

The corresponding *sodium* salt crystallises in golden-yellow platelets.

The *ammonium* salt of *dititani-o-cresotic acid*,

$$OTi_2(O{\cdot}C_7H_6{\cdot}CO_2)_6(NH_4)_4H_2,H_2O,$$

separates in well crystallised, yellowish-red prisms. E. F. A.

Aminoacetates of Phenols. CARL MANNICH and W. DRAUZBURG (*Arch. Pharm.*, 1912, **250**, 532—538).—A number of aminoacetates of phenols have been prepared by Delépine's method (Abstr., 1895, i, 327; 1897, i, 394) and their properties are described.

Phenyl iodoacetate, m. p. 68°, obtained by the interaction of sodium iodide and phenyl chloroacetate dissolved in acetone, crystallises from ether in colourless prisms, and with hexamethylenetetramine gives the *additive product*, $OPh{\cdot}CO{\cdot}CH_2(C_6H_{12}N_4)I$, m. p. 164° (decomp.), which when gently warmed with hydrochloric acid in alcohol yields *phenyl aminoacetate hydrochloride*, m. p. 206—208°, crystallising from acetone in colourless leaflets; the free ester decomposes immediately on liberation from its salts by alkalis.

Guaiacyl bromoacetate, $OMe{\cdot}C_6H_4O{\cdot}CO{\cdot}CH_2Br$, m. p. 45°, b. p. 181°/25 mm., obtained by the action of bromoacetyl bromide on guaiacol, crystallises from ether in colourless needles. It combines with hexamethylenetetramine, but gives an impure product containing the tetramine hydrobromide. *Guaiacyl iodoacetate*, m. p. 36°, obtained by treating the chloroacetate with sodium iodide in acetone, crystallises from ether in needles and decomposes when distilled even under reduced pressure. Its *additive product* with hexamethylenetetramine forms colourless leaflets, m. p. 157—158° (decomp.), and is hydrolysed by warm hydrochloric acid in alcohol to *guaiacyl aminoacetate hydrochloride*, m. p. 196°, which separates in colourless crystals; the free ester is an oil. *Eugenyl chloroacetate*, m. p. 23°, b. p. 187—193°/13 mm., was obtained by the action of chloroacetyl chloride on eugenol in presence of pyridine. o-*Nitrophenyl chloroacetate*, m. p. 63°, similarly prepared, crystallises in colourless needles, and gives no additive product with hexamethylenetetramine.

T. A. H.

Preparation of Complex Compounds from Halogenated Phenols and their Homologues. SCHÜLKE & MAYR and PAUL FLEMMING (D.R.-P. 247410).—When halogenated phenols or their homologues are boiled with an alkali hydroxide or carbonate in an anhydrous solvent (such as benzene), crystalline complex salts are formed; the patent describes the preparation of *compounds* from *p*-chloro-*m*-cresol, *p*-chloro- and *p*-bromo-phenols, and from 2 : 4 : 6-tribromophenol; these compounds find employment as disinfectants.

F. M. G. M.

Salts of Aminophenols with Dibasic Acids. ROBERT MEDINGER (*J. pr. Chem.*, 1912, [ii], **86**, 345—359. Compare Suida, Abstr., 1911, i, 284).—The author has examined the behaviour of the three isomeric aminophenols towards malic, tartaric, succinic, oxalic, and phthalic acids in aqueous or acetone solution, and finds that the tendency to form salts is most pronounced in the case of the ortho-compound, which yields only normal salts. With *m*- and *p*-aminophenols the acid salts are

formed most readily; only in a few cases could normal salts be isolated.

o-*Aminophenol tartrate*, $C_{16}H_{20}O_8N_2$, small, white needles (decomp. 211°), loses water at 180°, yielding the *compound*,

$$C_2H_2(OH)_2\left[C{<}{}^{N}_{O}{>}C_6H_4\right]_2.$$

The *acid tartrate* of *m*-aminophenol, $C_{10}H_{13}O_7N$, forms white needles (decomp. 175°); the para-isomeride is converted at 180—200° into p-*hydroxytartranil*, which forms slender, white, asbestos-like needles, m. p. above 250°. The normal *tartrate* of *p*-aminophenol decomposes at 220°.

The *acid malates* of *m*- and *p*-aminophenol decompose at 111° and 115° respectively; the *acid succinates* at 155° and 151°. The normal *succinate* of *o*-aminophenol (decomp. 144°) is resolved by crystallisation from water into its components.

Of the normal *oxalates*, the ortho-compound forms leaflets (decomp. 167·5°), the para-compound, lustrous, slender needles (decomp. 290°); the meta-compound decomposes at 180°, and the acid *oxalates* of *m*- and *p*-aminophenol at 176° and 220° respectively. The interaction of *o*-aminophenol and phthalic acid in hot aqueous solution yield the normal *phthalate*, m. p. 147·5°, and *di*-o-*hydroxyphthalanilide*, m. p. 227·5°.

The *acid phthalate* of *m*-aminophenol is transformed by boiling with water into m-*hydroxyphthalanil*, m. p. 220°; that of *p*-aminophenol (decomp. 250°) into p-*hydroxyphthalanil*, m. p. 250°.

Attempts to prepare additive compounds of the aminophenols with ethyl succinate and benzyl tartrate proved fruitless.

Benzyl tartrate is obtained as a viscid, yellow oil by heating benzyl alcohol and tartaric acid with potassium hydrogen sulphate at 130°. F. B.

Preparation of Pure *m*-Cresol. F. Hoffmann, La Roche & Co. (D.R.-P. 247272. Compare this vol., i, 549).—When commercial *m*-cresol (1000 parts) containing about 90% *m*- and 10% *p*-cresol is dissolved in 900 parts of concentrated sulphuric acid and sulphonated at a temperature below 100°, *m*-cresolsulphonic acid separates on cooling and can subsequently be converted into pure *m*-cresol. F. M. G. M.

Action of Oxygen on Quinol and a Sulphite. Johannes Pinnow (*Zeitsch. Wiss. Photochem.*, 1912, **11**, 289—304).—The changes which occur when oxygen is absorbed by aqueous solutions containing quinol and sodium sulphite have been investigated by quantitative measurements of the quinol, sulphite, and sulphate present at different stages of the oxidation process. Comparative experiments were also made with (1) quinol in the absence of sulphite; (2) potassium quinolmonosulphonate and sulphite; (3) potassium quinoldisulphonate and sulphite. From the data thus obtained it appears that, if sulphite is present in considerable excess, the quinol and sulphite disappear in the molar ratio 1 : 2. At the same time, one molecule of benzoquinonemonosulphonic acid and one of sulphate are produced. On the assumption

that the traces of copper present in the sulphite act catalytically, the changes which occur in the solutions may be represented by the equations: (1) $C_6H_4(OH)_2 + 2CuO = C_6H_4O_2 + Cu_2O + H_2O$; (2) $Cu_2O + O_2 = Cu_2O_3$; (3) $C_6H_4O_2 + Na_2SO_3 + H_2O = C_6H_3(OH)_2{\cdot}SO_3Na + NaOH$; (4) $Cu_2O_3 + Na_2SO_3 = Na_2SO_4 + 2CuO$; (5) $Cu_2O_3 + C_6H_4(OH)_2 = C_6H_4O_2 + 2CuO + H_2O$.

Although quinol in pure aqueous solution is not oxidised at a measurable rate, the increase in the hydroxyl ion concentration resulting from the addition of disodium phosphate is sufficient to cause the reaction to take place quite readily. If the quinol in the sulphite solution is replaced by its monosulphonate, the oxidation of the sulphite is retarded, and this is still more marked if the disulphonate is introduced. H. M. D.

Iron Compounds of Phenols. III. Iron Guaiacol Derivatives. Rudolf F. Weinland and Karl Binder (*Ber.*, 1912, **45**, 2498—2502. Compare this vol., i, 445).—By the reaction in alcoholic solution of ferric acetate, guaiacol, and alcoholic ammonia or alkali hydroxide, complex salts of a monobasic *tetraguaiacolferric acid* are obtained, having the constitution $[Fe(O{\cdot}C_6H_4{\cdot}OMe)_4]H$. In these, one guaiacol residue is attached by an auxiliary valency to the iron.

The *ammonium* salt forms a dark reddish-black, lustrous, crystalline powder, consisting of microscopic, rectangular prisms. The *sodium* salt forms a similar powder, composed of four- or six-sided microscopic plates, which are red or violet by transmitted light. The *potassium* salt appears under the microscope as bundles of four-sided prisms with straight cut ends.

These salts are stable when dry, but decomposed by boiling water.

Guaiacol reacts with anhydrous ferric chloride in ethereal solution to form a substance, $FeCl_2{\cdot}O{\cdot}C_6H_4{\cdot}OMe$. This constitutes a brownish-black powder of a dark bronze lustre, consisting of microscopic, well formed, transparent platelets. In alcohol it dissolves; at first blue, the solution then becomes deep green, and on the addition of more alcohol a dirty brown colour is produced. E. F. A.

Benzylamine Derivatives. Carl Mannich and R. Kuphal (*Arch. Pharm.*, 1912, **250**, 539—547).—The following substances were prepared in the course of various unsuccessful attempts to synthesise *iso*quinoline derivatives from substituted benzylamines, containing the skeleton $CH_2Ph{\cdot}CH_2{\cdot}NH{\cdot}\ddot{C}{\cdot}C\vdots$ (compare Fischer, Abstr., 1893, i, 427; Rügheimer and Schön, Abstr., 1909, i, 605).

Benzylmethylethanolamine, $CH_2Ph{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, b. p. 133—135°/14 mm., obtained by the action of ethylene chlorohydrin on benzylmethylamine in a closed vessel at 110°, is a colourless oil, yielding a crystalline *hydrochloride* and *platinichloride*, m. p. 173°. When heated with phosphoric oxide in a closed vessel at 200°, it gives *benzylvinylmethylamine*, the *hydrochloride* of which crystallises from a mixture of alcohol and ethyl acetate in colourless needles, m. p. 218—220°, and yields a *platinichloride*, m. p. 215—216° (decomp.), in orange-yellow leaflets.

3 : 4-*Methylenedioxybenzylethanolamine*,

$$CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot OH,$$

b. p. 198—205°/14 mm., similarly obtained, gives a *hydrochloride*, m. p. 150—151°, crystallising in colourless leaflets.

3 : 4-*Methylenedioxybenzylaminoacetal*,

$$CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH_2\cdot NH\cdot CH_2\cdot CH(OEt)_2,$$

b. p. 197—202°/12 mm., obtained by the action of chloroacetal on 3 : 4-methylenedioxybenzylamine at 140° in closed vessels, is a colourless liquid; the *hydrochloride*, m. p. 160° (decomp.), crystallises from dilute alcohol.

Benzyldichloroacetamide, $CH_2Ph\cdot NH\cdot CO\cdot CHCl_2$, m. p. 95—96°, obtained by the action of ethyl dichloroacetate on benzylamine, crystallises from dilute alcohol. 3 : 4-*Methylenedioxybenzyldichloroacetamide*, $CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH_2\cdot NH\cdot CO\cdot CHCl_2$, m. p. 136—137°, similarly prepared, crystallises in long, colourless needles from acetone or from dilute alcohol. *Benzylmethyldichloroacetamide*,

$$CH_2Ph\cdot NMe\cdot CO\cdot CHCl_2,$$

m. p. 63°, forms stellate groups of slender needles from dilute alcohol.

Oxamethane reacts at 0° with 3 : 4-methylenedioxybenzylamine to furnish the *compound*, $CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH_2\cdot NH\cdot CO\cdot CO\cdot NH_2$, small leaflets, m. p. 205—206°, and with benzylmethylamine to give the *substance*, $CH_2Ph\cdot NMe\cdot CO\cdot CO\cdot NH_2$, m. p. 86—87°, which crystallises from ether.

All attempts to condense these compounds to *iso*quinoline derivatives were unsuccessful. T. A. H.

Condensation of Chloroacetone with Phenols. EDUARD LIPPMANN (*Ber.*, 1912, 45, 2489—2491).—*Trihydroxy-αββ-triphenylpropane*, $CH_3\cdot C(C_6H_4\cdot OH)_2\cdot CH_2\cdot C_6H_4\cdot OH$, prepared by heating chloroacetone with three molecules of phenol and fuming hydrogen chloride, has been so far only obtained as a colloid, decomp. 175°. The *acetyl* derivative forms a colourless, lustrous mass, decomp. 155°.

Hexahydroxy-αββ-triphenylpropane, prepared in a similar manner from resorcinol, gives a colourless or faintly red-coloured substance, m. p. 180°. E. F. A.

Reduction of Disulphides by Dextrose. Preparation of Mercaptans. MAX CLAASZ (*Ber.*, 1912, 45, 2424—2828).—*oo*′-Dinitrodiphenyl disulphide is reduced to *o*-nitrophenyl mercaptan very easily and conveniently by heating an alcoholic suspension of the substance and dextrose with aqueous sodium hydroxide; by heating the alkaline solution with chloroacetic acid, an almost quantitative yield of *o*-nitrophenylthiolacetic acid is obtained (compare this vol., i., 389).

This method of reducing disulphides to mercaptans is apparently general; thus dithiosalicylic acid yields thiosalicylic acid, and diphenyl disulphide yields phenyl mercaptan, which readily yields phenylthiolacetic acid by condensation with chloroacetic acid in warm alkaline solution. C. S.

The Action of Light on Sulphoxides and Sulphides. OSCAR HINSBERG (*Ber.*, 1912, 45, 2337—2339).—The author withdraws his statement (Abstr., 1908, i, 257) as to the existence of an isomeric form of benzyl disulphide. Further experiments have hitherto failed to reveal the existence of isomeric disulphides other than those previously described.

A weak solution of β-naphthyl disulphide in acetic acid containing a trace of iodine, when exposed to direct sunlight for several weeks, gives a small amount of dinaphthylene disulphide, $C_{10}H_6<{S \atop S}>C_{10}H_6$ (compare Fries and Volk, Abstr., 1909, i, 406).

Benzyl sulphide under similar treatment in acetic acid solution also undergoes oxidation, giving a little benzyl sulphoxide. In this and the previous case the oxidation is attributed to the atmosphere.

Benzyl disulphoxide, if dissolved in acetic acid together with a little iodine, on exposure to sunlight is partly reduced to benzyl disulphide; the presence of the iodine as catalyst is essential to the action. D. F. T.

Sulphonylides. RICHARD ANSCHÜTZ (*Ber.*, 1912, 45, 2378—2380). —By the name *sulphonylides* the author designates a new class of cyclic esters of phenol-*o*-sulphonic acids.

o-Phenylenesulphonylide, $C_6H_4<{O\cdot SO_2 \atop SO_2\cdot O}>C_6H_4$, m. p. 236·5—237·5°, stout needles, is obtained by treating an ethereal solution of *o*-acetoxybenzenesulphonyl chloride with gaseous ammonia or with diethylamine.

Tolylene-3:4-sulphonylide, $C_6H_3Me<{O\cdot SO_2 \atop SO_2\cdot O}>C_6H_3Me$, m. p. 279—286°, is obtained in a similar manner, or, better, by treating *p*-cresol-3-sulphonic acid with phosphoryl chloride. These aromatic sulphonylides are very stable, but yield the alkali salts of phenolsulphonic acids by treatment with concentrated alkalis. C. S.

Aromatic Telluride Dihaloids and their Basic Fission Products. KARL LEDERER (*Annalen*, 1912, 391, 326—347).—Whilst diaryl telluride dihaloids, $TeAr_2X_2$, and the corresponding oxides, $TeAr_2O$, have long been known, the intermediate basic salts, $OH\cdot TeAr_2X$, have hitherto not been described. Diphenyl telluride dichloride, which is obtained almost quantitatively by passing oxygen through a mixture of its ethereal solution and concentrated hydrochloric acid, is converted by boiling water into basic *diphenyl telluride chloride*, $OH\cdot TePh_2Cl$, m. p. 233—234°, from which the *anhydride*, $O(TePh_2Cl)_2$, m. p. 233—234°, is obtained at 145—150°. Basic *diphenyl telluride bromide*, $OH\cdot TePh_2Br$, m. p. 264—265°, obtained from diphenyl telluride dibromide in a similar manner, yields the *anhydride*, $O(TePh_2Br)_2$, m. p. 264—265°, at 160—170°. *Diphenyl telluride di-iodide*, $TePh_2I_2$, m. p. 237—238° (decomp.), red crystals, obtained from diphenyl telluride and iodine in ether, is not converted by boiling water into the basic *iodide*. The latter, however, is obtained by treating a neutral solution of the basic

bromide or chloride with an alkali iodide. It is a canary-yellow, microcrystalline powder, m. p. 214—215°, easily decomposes into the oxide and di-iodide, and yields the *anhydride*, m. p. 216—217°, at 180°.

The following substances are also described: *Di*-p-*tolyl telluride dichloride*, m. p. 166—167°, monoclinic needles or triclinic leaflets; basic *di*-p-*tolyl telluride chloride*, m. p. 261—263°, and its *anhydride*, m. p. 261—263°; basic *di*-p-*tolyl telluride bromide*, m. p. 269—270°, and its *anhydride*; *di*-p-*tolyl telluride di-iodide*, m. p. 218—219°; basic *di*-p-*tolyl telluride iodide*, m. p. 203—204° (decomp.); *di*-p-*tolyl telluride oxide*, $(C_6H_4Me)_2TeO$, m. p. 166—167°; *di*-p-*tolyl telluride dihydroxide*, $(C_6H_4Me)_2Te(OH)_2$; *di*-o-*tolyl telluride dichloride*, m. p. 183°, and the basic *anhydride*, $O[TeCl(C_6H_4Me)_2]_2$, m. p. 220—222°; *di*-o-*tolyl telluride dibromide*, and the basic *anhydride*, m. p. 224—225° (decomp.); *di*-o-*tolyl telluride di-iodide*, m. p. 175—176°; *di*-o-*tolyl telluride oxide*, m. p. 205—206° (decomp.). C. S.

Synthesis of Tyrosol and its Conversion into Hordenine. FELIX EHRLICH and P. PISTSCHIMUKA (*Ber.*, 1912, **45**, 2428—2437).—Tyrosol is obtained in about 40% yield by the prolonged boiling of β-*p*-hydroxyphenylethylamine hydrochloride and an excess of potassium nitrite in neutral or faintly acid solution. It is obtained very conveniently as follows. β-*p*-Nitrophenylethylamine, readily obtained in 45% yield, together with 18% of the meta-isomeride, by the action of concentrated sulphuric acid and nitric acid, D 1·5, at −10° on β-phenylethylamine, is converted by potassium nitrite and 10% sulphuric acid into β-p-*nitrophenylethyl alcohol*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH$, m. p. 64°, yellow needles, which is then reduced by tin and hydrochloric acid. The resulting *hydrochloride*, m. p. 171°, of β-p-*aminophenylethyl alcohol* is converted by hydrochloric acid and potassium nitrite into β-*p*-hydroxyphenylethyl alcohol, which is identical with tyrosol.

Tyrosol has also been obtained, although in poor yield, by reducing β-*p*-nitrophenylethylamine hydrochloride to β-p-*aminophenylethylamine dihydrochloride*, m. p. about 296° (decomp.), and treating this with nitrous acid. Tyrosol (this vol., ii, 590) has b. p. 195°/18 mm., crystallises in the rhombic system, and reduces ammoniacal silver oxide solution, but not Fehling's solution, even by boiling. By heating with hydrochloric acid, D 1·19, at 100° for three hours, it yields β-*p*-hydroxyphenylethyl chloride, from which hordenine is obtained by the action of 33% alcoholic dimethylamine at 100° for three hours.

C. S.

Triphenylcarbinols. IV. HUGO KAUFFMANN and FELIX KIESER (*Ber.*, 1912, **45**, 2333—2337. Compare Kauffmann, this vol., i, 351, 397).—2 : 4 : 2′ : 4′-Tetramethoxy- and 2 : 4 : 2′ : 4′ : 2″ : 4″-hexamethoxytriphenylcarbinol are strongly basic substances, and exhibit halochromy in a marked manner.

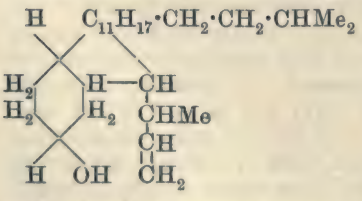
4-*Iodoresorcinol dimethyl ether*, m. p. 40°, b. p. 163°/14 mm., obtained by the action of iodine and mercuric oxide on resorcinol dimethyl ether, gives with magnesium and ether an organo-magnesium compound, which reacts with carbon dioxide, giving β-resorcylic acid, m. p. 108°, and with benzophenone giving 2 : 4-dimethoxytriphenylcarbinol

(compare Kauffmann and Pannwitz, Abstr., 1910, i, 393); in a similar manner, it reacts with 2 : 4-dimethoxybenzophenone, producing 2:4:2′:4′-*tetramethoxytriphenylcarbinol*, $OH\cdot CPh[C_6H_3(OMe)_2]_2$, m. p. 134·5°, which gives a bluish-red colour with acids, and then dyes wool pale red; the carbinol is reduced by zinc dust and acetic acid to 2 : 4 : 2′ : 4′-*tetramethoxytriphenylmethane*, $CHPh[C_6H_3(OMe)_2]_2$, colourless needles, m. p. 122°, which give an orange-red solution in concentrated sulphuric acid.

2:4:2′:4′:2″:4″-Hexamethoxytriphenylcarbinol, $OH\cdot C[C_6H_3(OMe)_2]_3$, obtained by the action of the above Grignard reagent on the dimethyl ether of ethyl β-resorcylate, and also in very small quantities as a by-product in the action of carbon dioxide on the same Grignard reagent, is a colourless, crystalline solid, m. p. 149°; it dissolves in dilute acids, giving a carmine-red solution which dyes wool red. It is reduced by zinc and acetic acid to 2 : 4 : 2′ : 4′ : 2″ : 4″-*hexamethoxytriphenylmethane*, m. p. 145°, which gives a red solution in concentrated sulphuric acid. D. F. T.

Cholesterol. XV. New Degradation Products of Cholesterol. Adolf Windaus (*Ber.*, 1912, 45, 2421—2423).—By oxidation with chromic acid in 20% sulphuric acid on the water-bath, a glacial acetic acid solution of the cyclic ketonic acid, $C_{24}H_{38}O_8$ (this vol., i, 449), yields a *lactone*, $C_{24}H_{36}O_3$ (the analyses agree better with the formula $C_{24}H_{38}O_3$), m. p. 140°, long needles subliming at about 280°/12 mm., which is neutral, unchanged by aqueous potassium hydroxide, and soluble in concentrated alcoholic potassium hydroxide. It forms an *oxime*, m. p. 136°, and is oxidised to a crystalline *acid*, m. p. 252°, by chromic acid.

The tricarboxylic acid, $C_{24}H_{38}O_6$, which is also produced by the oxidation of the acid, $C_{24}H_{38}O_8$ (*loc. cit.*), is oxidised by chromic, acetic, and 20% sulphuric acids to acetone and a *tetracarboxylic acid*, $C_{21}H_{30}O_8$ (or $C_{21}H_{32}O_8$), m. p. 185°, which contains a methyl group, since it yields acetaldehyde by oxidation with dilute sulphuric acid and potassium permanganate. At present the author is of opinion that cholesterol has the annexed formula. C. S.



Ferric Benzoates. Rudolf Friedrich Weinland and Alfred Herz (*Ber.*, 1912, 45, 2662—2680).—The amorphous, flesh-coloured precipitate obtained by mixing dilute aqueous solutions of sodium benzoate (1·5 mols.) and ferric chloride (0·5 mol.) consists of an impure *hexabenzoatotriferric monobenzoate*, (I) $\left[Fe_3{(OBz)_6 \atop (OH)_2}\right](OBz)$, which, when boiled with a solution of benzoic acid in acetone, separates as a lustrous, crystalline, dark reddish-orange powder, containing $2\frac{1}{2}H_2O$; it has also been obtained crystallised with $\frac{1}{2}H_2O$.

Hexabenzoatotriferric tribenzoate, $[Fe_3(OBz)_6](OBz)_3$, prepared by boiling the original monobenzoate (I) with a saturated solution of

benzoic acid in chloroform, crystallises in thin, microscopic, hexagonal, orange leaflets.

Extraction of the monobenzoate (I) for several days with benzene, which has been saturated at the ordinary temperature with benzoic acid, yields a *dibenzoate*, $\left[Fe_3{(OBz)_6 \atop (OH)}\right](OBz)_2$, crystallising in slender, light orange needles; if the extraction is carried out with an ethereal solution of benzoic acid, the dibenzoate is obtained in hexagonal, orange columns, containing $2H_2O$.

The following *compounds* of the mono- and di-benzoate are described: $\left[Fe_3{(OBz)_6 \atop (OH)}\right](OBz)_2,\left[Fe_3{(OBz)_6 \atop (OH)_2}\right](OBz)$, microscopic, orange-red, four-sided, hemimorphic columns;

$$\left[Fe_3{(OBz)_6 \atop (OH)}\right](OBz)_2,2\left[Fe_3{(OBz)_6 \atop (OH)_2}\right](OBz),2H_2O,$$

lustrous, yellowish-orange needles, and

$$\left[Fe_3{(OBz)_6 \atop (OH)}\right](OBz)_2,3\left[Fe_3{(OBz)_6 \atop (OH)_2}\right](OBz),6H_2O,$$

which crystallises in reddish-orange, rectangular plates or short columns.

Hexabenzoatotriferric perchlorate, $\left[Fe_3{(OBz)_6 \atop (OH)_2}\right]ClO_4,3H_2O$, is obtained in parallel aggregates of long, flat plates or columns by the interaction of the monobenzoate (I) and perchloric acid in aqueous alcoholic solution; by varying the conditions under which the reaction takes place, the following *compounds* were isolated: *hexabenzoatotriferric benzoate perchlorate*, $\left[Fe_3{(OBz)_6 \atop (OH)}\right]{ClO_4 \atop (OBz)},H_2O$, stout, red, hexagonal plates; $\left[Fe_3{(OBz)_6 \atop (OH)_2}\right]ClO_4,\left[Fe_3{(OBz)_6 \atop (OH)}\right]{ClO_4 \atop (OBz)},5H_2O$, which forms yellowish-orange, rhombic or hexagonal plates, and

$$2\left[Fe_3{(OBz)_6 \atop (OH)_2}\right]ClO_4,\left[Fe_3{(OBz)_6 \atop (OH)}\right]{ClO_4 \atop (OBz)},6H_2O,$$

crystallising in brown, hexagonal columns capped with pyramids.

The *platinichloride*, $\left[Fe_3{(OBz)_6 \atop (OH)_2}\right]_2PtCl_6,4H_2O$, crystallises in long, brown, rectangular plates.

The following *compounds* of the nitrate and nitrate benzoate were obtained by the action of nitric acid on the monobenzoate (I) in alcoholic and aqueous alcoholic solution respectively:

$$\left[Fe_3{(OBz)_6 \atop (OH)_2}\right]NO_3,\left[Fe_3{(OBz)_6 \atop (OH)}\right]{NO_3 \atop (OBz)},3H_2O,$$

stout plates of rhombohedric habit, and

$$3\left[Fe_3{(OBz)_6 \atop (OH)_2}\right]NO_3,\left[Fe_3{(OBz)_6 \atop (OH)}\right]{NO_3 \atop OBz},7H_2O,$$

which crystallises in parallel aggregates of reddish-yellow plates.

When boiled for several hours with acetone, the monobenzoate (I) loses benzoic acid, yielding *pentabenzoatotriferric monobenzoate*,

$$\left[Fe_3{(OBz)_5 \atop (OH)_3}\right](OBz),\tfrac{1}{2}H_2O,$$

which forms brownish-orange cubes, and has also been obtained

crystallised with $1H_2O$. The pentabenzoato-compound forms with hexabenzoatotriferric monobenzoate the *compounds*,

$$\left[Fe_3{(OBz)_5 \atop (OH)_3}\right](OBz),\left[Fe_3{(OBz)_6 \atop (OH)_2}\right](OBz),2H_2O$$

and $3\left[Fe_3{(OBz)_5 \atop (OH)_3}\right](OBz),\left[Fe_3{(OBz)_6 \atop (OH)_2}\right](OBz),H_2O$, and on treatment with chloroplatinic acid and perchloric acid is converted into the above-mentioned platinichloride and perchlorate of the hexabenzoato-base.

When boiled with 75% alcohol and the product crystallised from acetone, the original monobenzoate (I) yields *tribenzoatotriferric monobenzoate*, $\left[Fe_3 \begin{matrix}(OBz)_3 \\ O \\ (OH)_3\end{matrix}\right](OBz)$, which crystallises in dark brown, hexagonal columns capped with pyramids. F. B.

Preparation of Aminobenzoyl Compounds. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247818).—m-*Aminobenzoyl*-m-*nitroanilide*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2$, yellow crystals, m. p. 183°, is readily prepared from *m*-nitrobenzoyl-*m*-nitroanilide by reduction with sodium hydrogen sulphide in boiling 90% alcohol. F. M. G. M.

Hagemann's Esters and their Analogues. WALTER DIECKMANN (*Ber.*, 1912, **45**, 2689—2697).—Further insight into the isomerism exhibited by ethyl 2 : 6-diphenyl*cyclo*hexen-4-one-1-carboxylate (Abstr., 1911, i, 450) has been obtained by titration with bromine (Meyer, Abstr., 1911, i, 350; Meyer and Kappelmeier, *ibid.*, i, 832). Neither ketonic ester absorbs bromine in cold dilute alcoholic solution, whereas the enolic ester proves to be a mixture of the enolic and ketonic forms containing, when freshly prepared, 20—25% of the former. Similar experiments have been carried out with ethyl 6-phenyl-1-methyl-Δ^2-*cyclo*hexene-4-one-1-carboxylate, with the corresponding methyl ester and with ethyl 2-methyl*cyclo*hexene-4-one-1-carboxylate (Hagemann's ester).

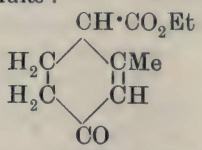
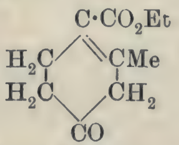
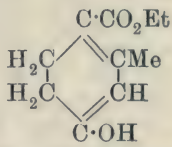
Ethyl 6-phenyl-2-methyl-Δ^1-*cyclo*hexene-4-one-1-carboxylate is transformed into ethyl 6-phenyl-2-methyl-Δ^2-*cyclo*hexene-4-one-1-carboxylate when boiled in alcoholic solution with sodium acetate and subsequently distilled. When dissolved in an alcoholic solution of sodium alkyloxide and poured into benzenediazonium acetate, it yields a *phenylhydrazone*, m. p. 98—99°.

Relationships between the isomerides are more readily observed with the corresponding methyl esters. *Methyl* 6-*phenyl*-2-*methyl*-Δ^2-cyclo*hexene* - 4 - *one* - 1 - *carboxylate*, colourless, prismatic needles, m. p. 89—90°, b. p. 220—225°/20 mm., is obtained by prolonged heating of a methyl-alcoholic solution of methyl benzylidenebisacetoacetate (m. p. 183°) with sodium methoxide or directly from the ethyl ester by means of methyl alcohol and sodium methoxide. It does not unite with bromine, and gives no coloration with ferric chloride. When heated at 150° or boiled in alcoholic solution during twelve hours, it only forms traces of the enolic ester. The *semicarbazone* has m. p. 183°. The ester is soluble in methyl-alcoholic sodium methoxide

with the formation of an intensely yellow *sodium* salt, which, on acidification, yields an impure enolic ester (containing from 10—20% of the enolic form). This solidified ester, after crystallisation from methyl alcohol, deposits the isomeric labile, ketonic ester (methyl 6-phenyl-2-methyl-Δ^1-*cyclo*hexene-4-one-1-carboxylate, m. p. 60°), which behaves towards ferric chloride and bromine in the same manner as the stable ester. The *semicarbazone*, m. p. 210°, is slowly formed when the aqueous alcoholic solution of the labile ester is mixed with semicarbazide acetate, a certain amount of transformation into the stable ester occurring simultaneously. Distillation or protracted heating of an alcoholic solution of the labile ester—particularly readily in the presence of alkaline reagents—produces an equilibrium mixture in which the stable ester predominates.

The *sodium* salt formed from the above ketonic esters readily couples with benzenediazonium acetate to form a *compound*, m. p. 102°.

With Hagemann's ester (ethyl 2-methyl-Δ^2-*cyclo*hexene-4-one-1-carboxylate, formula I) similar behaviour is observed (compare Hagemann, Abstr., 1893, i, 393; Callenbach, *ibid.*, 1897, i, 271; Rabe and Rahm, *ibid.*, 1905, i, 348; Merling, *ibid.*, 1905, i, 349). Neither the above ester nor the labile ketonic isomeride (formula II) contains more than a trace of the enolic form. By means of sodium methoxide, a *sodium* salt is obtained, which, on acidification, yields an ester mixture containing from 10—20% of the enolic form (formula III). The labile ester appears to be rather more readily soluble in alkali than the stable ester. Attempts to prepare isomeric semicarbazones were fruitless. γ-Acetobutyric acid is formed when either ester is oxidised by potassium permanganate. The relationships are shown in the following formulæ:

I. 
II. 
III. 

Apparently the keto-ester (II) formed from the enol ester readily passes into the keto-ester (I). Hence, probably, Callenbach's acid ester is a mixture of keto-ester (II) with varying amounts of keto-ester (I), whilst the neutral ester is either the keto-ester (I) or an equilibrium mixture of the two keto-esters in which the ester (I) is present in by far the greater quantity.

The sodium salt of the above esters readily couples with benzenediazonium acetate with the formation of a *phenylhydrazone*, m. p. 83—84°. H. W.

Alkylation of *cyclo*Hexanone-4-carboxylic Esters and the Constitution of the Menthenone Derived from Hagemann's Ester. WALTER DIECKMANN (*Ber.*, 1912, **45**, 2697—2707).—The menthenone derived from the *iso*propyl derivative of Hagemann's ester (see previous abstract) has been variously regarded as 1-methyl-2-*iso*propyl-Δ^6-*cyclo*hexene-5-one (Kötz and Auger, Abstr., 1911, i, 309)

and as 1-methyl-4-*iso*propyl-Δ^6-*cyclo*hexene-5-one (Merling and Welde, Abstr., 1909, i, 479). The author's views on the constitution of the enolic form of Hagemann's ester lead him to consider the ketone as 1-methyl-2-*iso*propyl-Δ^1-*cyclo*hexene-3-one. Attempts to obtain an insight into the mechanism of the alkylation of similar substances were not completely successful. Ethylation of ethyl 2 : 6-diphenyl-Δ^1-*cyclo*hexene-4-one-1-carboxylate gave a 40% yield of ethyl 2 : 6-diphenyl-3-ethyl-Δ^2-*cyclo*hexene-4-one-1-carboxylate, but action did not occur completely in one direction.

Ethyl 2 : 6-*diphenyl*-3-*ethyl*-Δ^2-cyclo*hexene*-4-*one*-1-*carboxylate*, needles, m. p. 102°, obtained by the action of ethyl iodide and alcoholic sodium ethoxide on ethyl 2 : 6-diphenyl-Δ^1-*cyclo*hexene-4-one-1-carboxylate, was slowly transformed by boiling mineral acids into 1 : 5-*diphenyl*-2-*ethyl*-Δ^1-cyclo*hexene*-3-*one*, needles, m. p. 102—103° (semicarbazone, m. p. 205°). The same ester was also obtained by elimination of water from *ethyl* 2 : 6-*diphenyl*-3-*ethyl*cyclo*hexane*-4-*one*-1-*carboxylate*, m. p. 150—160° (obtained from ethyl benzoylacetate and styryl propyl ketone (compare Abstr., 1911, i, 451).

Ethyl 2 : 4-*diphenyl*-1-*ethyl*-Δ^4-cyclo*hexene*-6-*one*-1-*carboxylate*, prisms, m. p. 138°, was obtained by the action of ethyl iodide on the sodio-salt of ethyl 2 : 4-diphenyl-Δ^4-*cyclo*hexene-6-one-1-carboxylate (obtained from phenyl styryl ketone and ethyl acetoacetate), or, in poor yield, by the action of sodium ethoxide on a mixture of phenyl styryl ketone and ethyl ethylacetoacetate. Boiling dilute sulphuric acid scarcely attacked it, but hydrochloric or hydrobromic acid in glacial acetic acid solution gradually transformed it into 2 : 4-*diphenyl*-1-*ethyl*-Δ^4-cyclo*hexene*-6-*one*, needles, m. p. 83° (semicarbazone, m. p. 208—209°).

Hagemann's ester was converted into the *iso*propyl derivative, from which the corresponding menthenone was obtained according to Callenbach's directions (Abstr., 1897, i, 271). Oxidation of the ketone by means of potassium permanganate yielded γ-acetobutyric acid (identified as semicarbazone) and *iso*butyric acid. The oxime, m. p. 104°, appeared in all respects identical with that obtained by Callenbach, but the oxime, m. p. 90—91°, described by Kötz and Auger (Abstr., 1911, i, 310) could not be isolated. Contrary also to the experience of the latter chemists, the hydrochloride of this oxime, m. p. 135°, was hydrolysed by water. Further discrepancies were also observed with regard to the semicarbazone, which according to Kötz and Auger (*loc. cit.*) occurs in two forms melting at 138° and 152° respectively. The author has observed only one semicarbazone, m. p. 167—168°, which could be preserved unchanged for months. H. W.

Combination of Phenolcarboxylic Acids. FERDINAND MAUTHNER (*J. pr. Chem.*, 1912, [ii], 86, 432).—A correction. The author has described (Abstr., 1911, i, 725; this vol., i, 267) a number of compounds obtained by the reaction of certain acid chlorides and phenolic esters in the presence of sodium hydroxide. It is now found that the phenolic esters take no part in the reaction, and therefore the compounds cannot have the structure previously assigned to them. F. B.

Sodium Phenyl Carbonate as an Intermediate Product in Kolbe's Synthesis of Salicylic Acid. S. TIJMSTRA (*Ber.*, 1912, 45, 2837—2838).—A reply to Sluiter (this vol., i, 189), re-stating and explaining the views already expressed (Abstr., 1905, i, 209, 439).

T. A. H.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. VII. Didepsides of Hydroxynaphthoic, Ferulic, and *o*-Coumaric Acids. Methyl Derivatives of Orsellic Acid. EMIL FISCHER and KURT HOESCH (*Annalen*, 1912, 391, 347—372).—*α-Methylcarbonato-β-naphthoic acid*,

$$CO_2Me\cdot O\cdot C_{10}H_6\cdot CO_2H,$$

m. p. 127—128° (decomp. corr.), is obtained by treating a cold suspension of α-hydroxy-β-naphthoic acid in benzene and dimethylaniline (2 mols.) with methyl chlorocarbonate and subsequently acidifying. The corresponding *chloride*, $CO_2Me\cdot O\cdot C_{10}H_6\cdot COCl$, m. p. 96°, colourless prisms, dissolved in acetone, is added to a solution of *p*-hydroxybenzoic acid in *N*-sodium hydroxide (2 mols.) at 0°; by acidification, the mixture yields 4-*α-methylcarbonatonaphthoyloxybenzoic acid*,

$$CO_2Me\cdot O\cdot C_{10}H_6\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

m. p. 231—232° (decomp. corr.). By hydrolysis in acetone by *N*-ammonium hydroxide (3 mols.), the latter yields 4-*α-hydroxynaphthoyloxybenzoic acid*, m. p. 247° (decomp. corr.).

The preceding method with acetone is the most convenient process for preparing didepsides, and has been employed in the following cases.

Methylcarbonatoferulic acid, $CO_2Me\cdot O\cdot C_6H_3(OMe)\cdot CH:CH\cdot CO_2H$, m. p. 186—187° (decomp. corr.), long needles, obtained from methyl chlorocarbonate and ferulic acid in cold alkaline solution, yields a *chloride*, $C_{12}H_{11}O_5Cl$, m. p. 147° (corr.), which forms with *p*-hydroxybenzoic acid by the acetone method 4-*methylcarbonatoferuloyloxybenzoic acid*, $CO_2Me\cdot O\cdot C_6H_3(OMe)\cdot CH:CH\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, m. p. 246° (decomp. corr.). The hydrolysis of the last by aqueous ammonia and pyridine yields 4-*feruloyloxybenzoic acid*, $C_{17}H_{14}O_6$, m. p. 233° (corr.), glistening leaflets. The preceding acid chloride reacts with ferulic acid in the acetone process to form *methylcarbonatodiferulic acid*, $CO_2Me\cdot O\cdot C_6H_3(OMe)\cdot CH:CH\cdot CO\cdot O\cdot C_6H_3(OMe)\cdot CH:CH\cdot CO_2H$, m. p. 230° (decomp. corr.), the hydrolysis of which yields *diferulic acid*, $C_{20}H_{18}O_7$, m. p. 241—242° (decomp. corr.). *Methylcarbonatodi-o-coumaric acid*, $CO_2Me\cdot O\cdot C_6H_4\cdot CH:CH\cdot CO\cdot O\cdot C_6H_4\cdot CH:CH\cdot CO_2H$, m. p. 170° (corr.), obtained in a similar manner from *o*-coumaric acid and methylcarbonatocoumaroyl chloride, yields *di-o-coumaric acid*, m. p. 188° (decomp. corr.), by hydrolysis with aqueous ammonia.

2-*Methylcarbonato*-3-*naphthoic acid*, $CO_2Me\cdot O\cdot C_{10}H_6\cdot CO_2H$, m. p. 174—175° (decomp. corr.), forms a *chloride*, $C_{13}H_9O_4Cl$, m. p. 107° (corr.), which does not yield a didepside by the acetone method, but condenses with 2-hydroxy-3-naphthoic acid in benzene in the presence of dimethylaniline to form 2 : 2′-*methylcarbonato*-3′-*naphthoyloxy*-3-*naphthoic acid*, $CO_2Me\cdot O\cdot C_{10}H_6\cdot CO\cdot O\cdot C_{10}H_6\cdot CO_2H$, m. p. 215° (decomp. corr.); the hydrolysis of the latter by aqueous ammonia and

acetone yields *di-2-hydroxy-3-naphthoic acid*,

$$OH\cdot C_{10}H_6\cdot CO\cdot O\cdot C_{10}H_6\cdot CO_2H,$$

m. p. 245° (decomp. corr.).

Orsellinic acid and methyl chlorocarbonate (1·1 mol.) in cold *N*-sodium hydroxide (2 mols.) yield *methylcarbonato-orsellinic acid* (*5-methylcarbonato-3-hydroxy-o-toluic acid*),

$$CO_2Me\cdot O\cdot C_6H_2Me(OH)\cdot CO_2H,$$

m. p. 153—154° (corr.), which is converted by further treatment with sodium hydroxide and methyl chlorocarbonate into *dimethylcarbonato-orsellinic acid*, $C_{12}H_{12}O_8$, m. p. 133° (decomp. corr.). All attempts to prepare the chloride of the latter acid have been unsuccessful, so that the synthesis of lecanoric acid (orsellic acid), the longest known lichen acid, has been frustrated.

Methyl methylcarbonato-orsellinate, $CO_2Me\cdot O\cdot C_6H_2Me(OH)\cdot CO_2Me$, m. p. 80—81° (corr.), is obtained from methyl orsellinate and methyl chlorocarbonate in alkaline solution. Like the preceding methylcarbonato-derivative, it develops a reddish-violet coloration with alcoholic ferric chloride.

Orsellinic acid is generally regarded as 3 : 5-dihydroxy-*p*-toluic acid. The authors are of opinion that it is 3 : 5-dihydroxy-*o*-toluic acid for the following reasons. Diazomethane methylates phenolcarboxylic acids preferentially in the para-position; ethyl orsellinate and ethereal diazomethane yield an *a-methyl ether*, $CO_2Et\cdot C{<}{\begin{smallmatrix}C(OH)\cdot CH\\ CMe{:}CH\end{smallmatrix}}{>}C\cdot OMe$, m. p. 72—75°, which gives with ferric chloride a reddish-violet coloration resembling that developed by salicylic acid. Also methyl chlorocarbonate attacks phenolcarboxylic acids preferentially in the para-position. The preceding methyl methylcarbonato-orsellinate, therefore, has the methylcarbonato-group in position 5, and consequently develops a characteristic coloration with ferric chloride. Now, when methylcarbonato-orsellinic acid is treated with ethereal diazomethane, it yields *methyl methylcarbonato-orsellinate-β-methyl ether*, $CO_2Me\cdot C{<}{\begin{smallmatrix}C(OMe)\cdot CH\\ CMe{:}CH\end{smallmatrix}}{>}C\cdot O\cdot CO_2Me$, m. p. 86° (corr.), which does not develop a coloration with ferric chloride. The hydrolysis of the ester by concentrated sulphuric acid at 25° yields *methylcarbonato-orsellinic acid-β-methyl ether*, $CO_2H\cdot C{<}{\begin{smallmatrix}C(OMe)\cdot CH\\ CMe{:}CH\end{smallmatrix}}{>}C\cdot O\cdot CO_2Me$, m. p. 145° (corr.), which also does not develop a coloration with ferric chloride. The hydrolysis of the last substance by *N*-sodium hydroxide yields *orsellinic acid-β-methyl ether*, $CO_2H\cdot C{<}{\begin{smallmatrix}C(OMe)\cdot CH\\ CMe{:}CH\end{smallmatrix}}{>}C\cdot OH$ (decomp. 175°), which develops a yellowish-red coloration with ferric chloride. Were the old formula of orsellinic acid correct, the β-methyl ether would be a derivative of salicylic acid, and should develop its characteristic coloration with ferric chloride; moreover, the α- and the β-methyl ethers would be identical, not isomeric, as is actually the case.

Orsellinic acid-α-methyl ether is shown to be identical with everninic acid by direct comparison of the m. p., colorations with ferric chloride, crystalline form, and properties of the ethyl esters. C. S.

Number of Isomerides of Merotropic and Desmotropic Compounds. IV. Isomeric Modifications of Ethyl Formylphenylacetate. ARTHUR MICHAEL (*Annalen*, 1912, **391**, 235—274).—The author has re-commenced an investigation of the α-, β-, and γ-modifications of ethyl formylphenylacetate, since the constitutions of the first two, and the existence of the last, are still subjects of discussion. According to the author, ethyl formylphenylacetate exists in three modifications: the α-ester, b. p. 125—126°/9 mm. (decomp.), β-ester, m. p. about 40°, and γ-ester, m. p. about 100°. All of these are enolic, since they react with aliphatic tertiary amines (compare Michael and Smith, Abstr., 1908, i, 943), and also with phenylcarbimide; in the latter case, all three yield the carbanilide, m. p. 117—118° (Abstr., 1906, i, 179), the α-ester giving, in addition, an *isomeride*, $C_{18}H_{17}O_4N$, m. p. 59°, which is converted quantitatively into the anilide, m. p. 117—118°, by heat.

The preparation of α-, β-, and γ-ethyl formylphenylacetates requires great care, and the original paper must be consulted for details. Briefly, they are obtained as follows. Ethyl formate and ethyl phenylacetate in ether are treated with sodium according to Wislicenus' directions. The aqueous extract of the product is freed from ether by air, kept at 0° for three to four hours, acidified by sulphuric acid, D at least 1·36, and the mixture kept at 0° for about four hours before removing the precipitated γ-ester.

The β-ester is obtained by passing carbon dioxide into the preceding aqueous alkaline extract, and keeping the product at 0° for some hours. The solid, m. p. 44—54°, is dissolved in dilute potassium hydroxide at 0°, and carbon dioxide is passed immediately through the solution; once again the mixture is kept at 0° for some hours before the β-ester is removed.

The liquid α-ester is obtained by Wislicenus' method, and is purified through the copper derivative. The ester must be heated at 120° in a sealed tube for two to three hours, and subsequently distilled in a vacuum in order to obtain a product free from the solid modifications. The α-ester cannot be kept without isomerising; in air, it undergoes a profound change, and finally does not develop a coloration with alcoholic ferric chloride.

The β- and the γ-ester change to the α- by fusion. Neither gives directly a coloration with ferric chloride, but does so after being kept in solution for some time (change to the α-modification).

Wislicenus' β-modification, m. p. about 70°, is most probably a mixture of the two preceding solid modifications. C. S.

Number of Isomerides of Merotropic and Desmotropic Compounds. V. Isomeric Enolic Modifications of Ethyl Formylphenylacetate. ARTHUR MICHAEL and G. PRESCOTT FULLER (*Annalen*, 1912, **391**, 275—308. Compare preceding abstract).—α-Ethyl formylphenylacetate is recovered unchanged after being kept for a short time in methyl or ethyl alcohol, but, after prolonged keeping, an additive compound of the ester and the alcohol is obtained, which does not develop a coloration with ferric chloride. The β- and the γ-esters yield apparently the same additive compound after

prolonged keeping in either of these solvents; when rapidly recovered, however, each is obtained as a mixture of both.

The α-ester is recovered unchanged from most solvents; a transitory formation of a solid mixture is observed in acetone, methylal, or pinacolin. The β-ester changes to the α in most solvents, even in the cold; in bromoform, it changes almost completely to the γ-ester within fifteen minutes, the α-ester being finally obtained after prolonged keeping. The γ-ester changes to the α in all solvents.

The preceding results show that, contrary to the opinion of Wislicenus, there is no simple relation between the dielectric constant of an organic solvent and its capacity of producing isomerisation of one form of ethyl formylphenylacetate into another.

Mixtures of the solid β- and γ-esters in known proportions give an m. p. curve which indicates that the substances, m. p. about 50° and about 70° respectively, which are so frequently isolated in the preparation of the various modifications of ethyl formylphenylacetate, are not individual; these substances and the corresponding artificial mixtures behave alike physically.

The molecular weight of the γ-ester in cold benzene indicates that the compound is unimolecular. The determination of the molecular weight of the β-ester is difficult, because the substance changes so rapidly to the γ-ester in solution. Experiments on a sample, m. p. 55°, in benzene and in acetic acid gave values corresponding with the unimolecular formula, whilst the % of γ-ester had increased by only about 20% during the estimation.

The action of sodium ethoxide on an ethereal solution of the α-ester gives a homogeneous α-sodium derivative. When this solid is acidified with sulphuric acid, an oily ester is obtained, together with a little solid ester. By acidifying a cold dilute aqueous solution of the α-sodium derivative, the oil obtained solidifies the more rapidly the greater is the concentration of the acid used. The m. p. of the solidified oil is 90—100°, and is independent of the concentration of the acid. Excepting phosphoric and oxalic acids, there is an approximate relation between the % of γ-ester in the solidified oil and the affinity constant of the acid used in precipitating it.

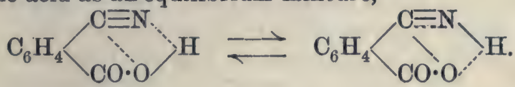
The sodium derivative, whether solid or in aqueous solution, yields the bluish-violet ferric salt with ferric chloride. The α-ester and alkaline copper acetate give at once the green α-copper derivative, which is also obtained, more slowly, from the β- and the γ-esters. The bluish-green precipitate obtained from the α-sodium salt and cold aqueous copper sulphate is a mixture of an inorganic copper salt, the green α-copper derivative, and an oil. Copper chloride also produces the green α-derivative; cuprous chloride gives a green precipitate, from which a mixture of the liquid and solid esters is obtained by acidification with sulphuric acid. These results do not support the theory of the existence of isomeric metallic derivatives of ethyl formylphenylacetate. C. S.

The Lactone of α-o-Methoxyphenyl-o-hydroxy-p-tolylacetic Acid. H. STOCKMANN (*Ber.*, 1912, 45, 2547—2548).—The divergence of the m. p. (116—119°) given for the above substance by Stoermer

and Friemel (this vol., i, 45) from that given by earlier workers (120—121°) is due to impurity arising from the presence of *p*-cresol in the *m*-cresol used. A carefully purified specimen of *m*-cresol when treated by Stoermer and Friemel's method gave a product of the higher m. p. D. F. T.

o-Cyanobenzoic Acid. JOHANNES SCHEIBER [and, in part, A. DEUTSCHLAND] (*Ber.*, 1912, **45**, 2398—2403).—Several investigators have prepared *o*-cyanobenzoic acid by methods which leave no doubt as to its constitution. However, the acid behaves abnormally in several respects. For example, its dissociation constant is, contrary to expectation, smaller than that of *o*-chlorobenzoic acid, its tendency to liberate iodine from an iodide-iodate mixture is less than that of the weaker *m*-cyanobenzoic acid, and the absorption spectra of *o*- and of *m*-cyanobenzoic acids exhibit differences which are not found in the spectra of other *o*- and *m*-substituted benzoic acids.

The author is of opinion that these abnormalities can be explained by assuming a more intimate connexion between the cyano- and the carboxyl groups than is indicated by the ordinary formula, and represents the acid as an equilibrium mixture,



C. S.

Fluorescence in the Terephthalic Acid Series. HUGO KAUFFMANN and LEOPOLD WEISSEL (*Annalen*, 1912, **393**, 1—29).—Continuing their investigations of the auxochromic influence of nitrogen in fluorescent substances, the authors find that, whilst methyl terephthalate is not fluorescent even in the ultra-violet, methyl aminoterephthalate and the 2 : 5- and 2 : 6-diamino-esters are fluorescent in the solid state and in solution. The phenomenon is due to the auxochromic influence of the amino-group, because, whilst the preceeding diamino-esters fluoresce in the orange, the fluorescent band shifts towards the violet when the amino-groups are replaced by weaker auxochromes; thus methyl 2 : 5-dihydroxyterephthalate and 2 : 5-dimethoxyterephthalate fluoresce respectively in the blue and the violet. An alkaline alcoholic solution of the dihydroxy-ester fluoresces orange, because the auxochromic character of the hydroxyl groups is strengthened by salt formation. Methyl aminoterephthalate shows yellow fluorescence in the solid state and violet blue in solution; its acetyl derivative fluoresces blue in the solid state and violet in solution. Here again is illustrated the shift of the fluorescent band towards the violet when the auxochromic character of the amino-group is weakened by acetylation. Other examples of the same kind are quoted.

The orientation of the auxochromes also has a great influence on the fluorescence; amongst other examples, the fact is mentioned that the fluorescent band of methyl 2 : 6-diaminoterephthalate in any solvent is always nearer the violet than that of the 2 : 5-diamino-ester in the same solvent.

The influence of the solvent on the fluorescence is particularly

marked in the case of methyl 2:6-diaminoterephthalate. A comparison of many examples shows that the change in the fluorescent colour produced by a solvent is greater the more marked is the auxochromic character of the group causing the fluorescence. An important deduction from this is that the solvent must have some influence on the auxochromic group. The fluorescent colour of a substance is deepened most by dissociating solvents. Thus methyl 2:6-diaminoterephthalate, which exhibits a green or greenish-yellow fluorescence in hexane, benzene, ether, or chloroform, fluoresces orange-yellow in pyridine and orange in alcohol, acetic acid, or *iso*butyl alcohol. Carbon disulphide is remarkable in that substances which exhibit intense fluorescence in other solvents, show a scarcely appreciable fluorescence in this solvent.

Methyl dimethylaminoterephthalate is remarkable in that it is non-fluorescent in almost all solvents. In hexane, carbon tetrachloride, and perchloroethylene it exhibits a violet to blue fluorescence. The authors are of opinion that this ester may be used to ascertain the character of a solvent; any solvent in which it forms a fluorescent solution is a non-dissociating, indifferent solvent. Such, for example, is tin tetra-ethyl, in which the ester shows a feeble blue fluorescence.

Methyl 2:5-diaminoterephthalate is easily obtained as follows. Methyl terephthalate is nitrated by fuming sulphuric and nitric acids below 5°. The resulting methyl nitroterephthalate, m. p. 76°, which is freed from a little accompanying *methyl dinitrohydroxyterephthalate*, $OH\cdot C_6H(NO_2)_2(CO_2Me)_2$, m. p. 124°, by treatment with aqueous sodium carbonate, is reduced by stannous chloride and 25% methyl alcoholic hydrogen chloride to methyl aminoterephthalate, the acetyl derivative of which is then nitrated by fuming nitric and concentrated sulphuric acids at about 0°. The main product is *methyl 2-nitro-5-acetylaminoterephthalate*, m. p. 142°, yellow prisms, which is non-fluorescent; the by-product, m. p. 128°, is probably *methyl 3-nitro-5-acetylaminoterephthalate*, but it has not been obtained free from the preceding isomeride. By hydrolysis with boiling methyl-alcoholic sulphuric acid, methyl 2-nitro-5-acetylaminoterephthalate yields *methyl 2-nitro-5-aminoterephthalate*, m. p. 187° (the corresponding *acid* has decomp. about 260°), the reduction of which by stannous chloride and methyl-alcoholic hydrogen chloride yields *methyl 2:5-diaminoterephthalate*, m. p. 185°, long, orange-red prisms. This ester exhibits a magnificent orange fluorescence in the solid state, and forms a *dibenzoyl* derivative, m. p. 268° (bluish-green fluorescence in solid state viewed through a blue screen; violet to blue fluorescence in solution), *acetyl* derivative, m. p. 198°, yellow needles (faint orange-yellow fluorescence in solid state; blue to green fluorescence in solution), *diacetyl* derivative, m. p. 284°, pale yellow needles (faint yellow fluorescence in solid state: violet to blue fluorescence in solution), and *benzoylacetyl* derivative, m. p. 248°, pale yellow crystals. *Methyl 5-amino-2-hydroxyterephthalate*, m. p. 144°, obtained by the electrolytic reduction of methyl nitroterephthalate in sulphuric acid and subsequent esterification, forms deep yellow crystals, which exhibit a faint yellow fluorescence behind a blue screen, and yields bluish-green to yellowish-green fluorescent solutions.

2 : 6-Diamino-*p*-toluic acid, which is obtained free from any isomeride by the reduction of 2 : 6-dinitro-*p*-toluic acid by tin and concentrated hydrochloric acid, forms a *methyl* ester, m. p. 129°, brown crystals, which exhibits peculiar fluorescent phenomena on account of the orientation of the amino- and the carbomethoxy-groups. Solutions of the ester in alcohol, acetic acid, petroleum, ether, or benzene are non-fluorescent. By treating its alcoholic solution with a little mineral acid, an intense violet-blue fluorescence is produced, which disappears by the addition of an excess of acid.

2 : 6-*Diacetylamino*-p-*toluic acid*, m. p. above 280°, colourless needles, dissolved in water containing sodium carbonate, is treated with magnesium sulphate and then heated with potassium permanganate. The resulting 2 : 6-*diacetylaminoterephthalic acid*, m. p. above 280°, yields by boiling with methyl alcoholic hydrogen chloride, *methyl* 2 : 6-*diaminoterephthalate*, $C_6H_2(NH_2)_2(CO_2Me)_2$, m. p. 162°, yellow crystals, solutions of which exhibit intense violet to green fluorescence. Its *diacetyl* derivative, m. p. 204°, shows a faint blue fluorescence in the solid state and forms violet to blue fluorescent solutions. The *dibenzoyl* derivative, m. p. 248°, fluoresces greenish-white in the solid state and violet in solution.

Methyl aminoterephthalate reacts abnormally in some respects. It does not react with benzaldehyde, and only very slowly with phenylthiocarbimide, yielding the *thiocarbanilino*-derivative,

$$NHPh\cdot CS\cdot NH\cdot C_6H_3(CO_2Me)_2,$$

m. p. 211°, which is not fluorescent in solution. By treating its diazotised solution with alkaline β-naphthol, *methyl* 2-β-*naphtholazoterephthalate*, $C_6H_3(CO_2Me)_2\cdot N_2\cdot C_{10}H_6\cdot OH$, red needles, is obtained, which is not fluorescent.

By heating with methyl sulphate on the water-bath, methyl aminoterephthalate yields a mixture of methyl dimethylaminoterephthalate, m. p. 70·5° (Wegscheider and Black give 66—68° : this vol., i, 263), and methyl methylaminoterephthalate, m. p. 93° (not 89—90° : *loc. cit.*), which is separated by converting the latter into its *nitroso*-compound, m. p. 80°. C. S.

Phenolphthalein and its Colourless Salts. III. Preparation of Monobasic Phenolphthalates. PHILIP A. KOBER, J. THEODORE MARSHALL, and E. N. ROSENFELD (*J. Amer. Chem. Soc.*, 1912, **34**, 1424—1433. Compare Abstr., 1911, i, 300, 984).—The dynamics of phenolphthalein reactions are discussed, and the conclusion is drawn that in ordinary phenolphthalein the quinonoid dibasic salt is essentially primary and the carbinol form secondary.

Potassium phenolphthalate,

$$\begin{matrix}CO_2K\cdot C_6H_4\\ OH\end{matrix}{>}C{<}\begin{matrix}C_6H_4\cdot OH\\ C_6H_4\cdot OH\end{matrix}, H_2O, C_2H_5\cdot OH,$$

may be prepared by passing carbon dioxide into a solution of the tripotassium salt in absolute alcohol, filtering the product, and precipitating with dry ether. The corresponding *sodium* salt can be obtained in the same manner. These monobasic salts crystallise in long, colourless, hexagonal prisms with truncated ends, and are slowly hydrolysed by water at the ordinary temperature with the develop-

ment of colour and the separation of phenolphthalein. When the salts are crystallised from acetone, the alcohol of crystallisation is wholly, or in part, replaced by the former solvent. E. G.

Crystallographic Study of 3 : 4 : 5-Trimethoxyphthalic Acid. Aristide Rosati (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 358—359).—This acid of m. p. 174° (decomp.) (compare Bargellini and Molina, this vol., i, 773) crystallises in the pinacoidal class of the triclinic system [$a : b : c = 0{\cdot}3728 : 1 : 0{\cdot}2994$, α 77°4′, β 111°32′, γ 134°40′]. R. V. S.

Ketoaldehydes. Mercaptals of Benzoyl- and Thienoylacetaldehyde. C. Kelber and A. Schwarz (*Ber.*, 1912, 45, 2484—2489).—The *ethylene mercaptal* of *benzoylacetaldehyde*,

$$COPh{\cdot}CH_2{\cdot}CH{<}\begin{matrix}S{\cdot}CH_2\\ |\\ S{\cdot}CH_2\end{matrix},$$

prepared by condensing the components in presence of hydrogen chloride, crystallises in thin, colourless platelets, m. p. 80°, which become brown on exposure to light.

Benzoylacetaldehyde ethyl mercaptal, $COPh{\cdot}CH_2{\cdot}CH(SEt)_2$, crystallises in thin, colourless needles, m. p. 46—47°.

Thienoylacetaldehyde, $CH{<}\begin{matrix}CH{\cdot}CH\\ \quad\ \ \|\\ S{-}{-}C{\cdot}CO{\cdot}CH_2{\cdot}CHO\end{matrix}$, obtained by condensing thienyl methyl ketone and ethyl formate by means of sodium ethoxide, is a viscid, yellow oil. The *sodium* salt, which is stable when dry, gives a deep red coloration with ferric chloride. In aqueous solution it gives precipitates with calcium, strontium, and magnesium chlorides, and also with mercuric chloride. The *mono-oxime* crystallises in flat tablets of silvery lustre, m. p. 106—107°. In solution a yellow coloration is obtained with ferric chloride, which is changed to blue on adding sodium acetate.

Thienoylacetaldehyde ethylene mercaptal,

$$CH{<}\begin{matrix}CH{\cdot}CH\\ \quad\ \ \|\\ S{-}{-}C{\cdot}CO{\cdot}CH_2{\cdot}CH\end{matrix}{<}\begin{matrix}S{\cdot}CH_2\\ |\\ S{\cdot}CH_2\end{matrix},$$

crystallises in stunted crystals, m. p. 98—99°.

When thienoylacetaldehyde is left overnight, it condenses to *trithienoylbenzene*, $C_6H_3(CO{\cdot}C_4H_3S)_3$, the oil becoming converted into a reddish-yellow mass. The purified crystals form flat needles, m. p. 212—213°. E. F. A.

Reduction of Δ^{α}-Ketones and Formation of Indene Derivatives. Johannes Thiele and P. Ruggli (*Annalen*, 1912, 393, 61—80).—By reducing unsaturated ketones of the type $CHR{:}CH{\cdot}COR'$ with zinc dust and a mixture of acetic anhydride, acetic acid, and concentrated sulphuric acid, the authors have obtained evidence of the intermediate production of compounds of the type $CH_2R{\cdot}CH{:}CR'{\cdot}OH$.

Phenyl styryl ketone, anisylideneacetophenone, and benzylidenedeoxybenzoin have been examined. The usual reducing agents convert these normally into the saturated ketones, but with the preceding mixture at or below 0° the following results have been obtained.

Phenyl styryl ketone yields a brown mass, from which have been isolated a little $\alpha\delta$-dibenzoyl-$\beta\gamma$-diphenylbutane and a *substance*, $C_{30}H_{24}O$, m. p. 168—169°, yellow powder, which is probably 2-*benzoyl*-1 : 3 : 4-*triphenyl*-Δ^1-cyclo*pentene*, produced from the former by loss of water. By treatment with the preceding reducing mixture, benzylidenedeoxybenzoin yields a mixture of substances. The same mixture is also obtained in the absence of zinc dust, so that the reaction is one of addition of acetic acid (or anhydride), not of hydrogen. By a tedious fractional crystallisation from glacial acetic acid, three *substances* have been isolated from the mixture. Two of these, $C_{23}H_{18}O_2$, m. p. 170—172°, and $C_{23}H_{20}O_3$, m. p. sharply between 140° and 171° (decomp.), according to the conditions of heating, are substances of unknown constitution, but the third, $C_{23}H_{18}O_2$, m. p. 166—167°, is 1-*acetoxy*-2 : 3-*diphenylindene*, $C_6H_4<\begin{matrix}CH(OAc)\\ \overline{\quad\quad} CPh\end{matrix}>CPh$. This substance is produced as the result of the intermediate formation of

OAc·CHPh·CPh:CPh·OH,

not OAc·CHPh·CHPh·COPh, from benzylidenedeoxybenzoin and acetic acid, because the second substance, *acetoxybenzyldeoxybenzoin*, m. p. 127·5—128·5°, colourless prisms, obtained from bromobenzyldeoxybenzoin and silver acetate, is not converted into an indene derivative by concentrated sulphuric acid either alone or mixed with acetic acid and acetic anhydride. *Bromobenzyldeoxybenzoin*,

CHPhBr·CHPhBz,

m. p. 158° (decomp.), colourless needles, is obtained by treating a cold solution of benzylidenedeoxybenzoin in acetyl bromide with a little concentrated sulphuric acid; its constitution follows from the fact that it is reconverted into benzylidenedeoxybenzoin by boiling pyridine.

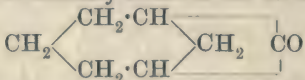
By treatment with hydrogen bromide in glacial acetic acid at 100°, 1-acetoxy-2 : 3-diphenylindene is converted into 1-*bromo*-2 : 3-*diphenylindene*, $C_6H_4<\begin{matrix}CHBr\\ -CPh\end{matrix}>CPh$, decomp. 158°, yellow crystals, from which the acetate is regenerated by silver acetate.

By reduction with zinc dust and glacial acetic acid at 50—80°, 1-bromo-2 : 3-diphenylindene yields 2 : 3-*diphenylindene*, m. p. 108—109°, almost colourless prisms, which develops an intense dark green coloration with concentrated sulphuric acid and forms an *oximino*-compound, $C_6H_4<\begin{matrix}C(:NOH)\\ \overline{\quad\quad} CPh\end{matrix}>CPh$, m. p. 253—255° (decomp.), yellowish-brown prisms, by treatment with amyl nitrite and alcoholic sodium ethoxide; the same substance is obtained from diphenylindone and hydroxylamine, and yields diphenylindone by treatment with hydrogen bromide in glacial acetic acid containing a little copper oxide. C. S.

Constitution of Phenyl-*o*-nitroindone [4-Nitro-2-phenylindone] and of its Ozonide. MARUSSIA BAKUNIN and T. ANGRISANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1912, [iii], 18, 213—222. Compare Bakunin, this vol., i, 344).—The ozonisation of the nitrophenylindone in chloroform solution has been repeated with ozonised oxygen (7%). The ozonide of m. p. 157—158° previously mentioned

was obtained, together with benzoic acid and ethyl 3-nitro-2-aldehydobenzoate, m. p. 133°. The two last-named substances are also obtained when the ozonide is subjected to prolonged boiling with water, alcohol or sodium carbonate, and this confirms the constitution previously assigned to it. The formation of this ozonide confirms the presence of a double linking in the phenylnitroindone. R. V. S.

Synthesis of Meta-bicyclic Systems. Synthesis of a Demethylated Pinone. OTTO STARK (*Ber.*, 1912, **45**, 2369—2374).—*cyclo*Hexene-1 : 3-dicarboxylic acid is readily obtained in quantity by reducing *iso*phthalic acid with sodium amalgam by Baeyer and Villiger's method to the tetrahydro-acid, and then treating an aqueous solution of this easily soluble acid with hydrogen and colloidal palladium as in the Paal-Skita process. From the product, the *cis*-anhydride is obtained by means of acetyl chloride, and converted into calcium *cis-cyclo*hexenedicarboxylate. By distillation in a current of carbon dioxide, the finely powdered salt yields a liquid, the fraction, b. p. 60—100°/18 mm., of which contains a *ketone*, $C_7H_{10}O$, b. p. 157—158° (decomp.) or 60—70°/18 mm., D^{20} 0·9322, n_D^{20} 1·4731 (*semicarbazone*, m. p. 179—180°), which provisionally receives the formula :



on account of its exalted molecular refraction. The ketone is attacked substitutively by bromine, and is not stable to alkaline potassium permanganate. C. S.

Alkylation of Benzoylacetone and Desmotropy of Methyl- and Ethyl-benzoylacetone. WALTER DIECKMANN (*Ber.*, 1912, **45**, 2685—2689).—Previous attempts to alkylate benzoylacetone have led to the isolation of the decomposition products of the alkyl derivatives (Claisen and Lowman, Abstr., 1888, 692; Auwers, this vol., i, 486). The author shows that the methyl and ethyl derivatives may be readily prepared by use of the corresponding alkyl iodides if excess of sodium alkoxide is carefully avoided.

Methylbenzoylacetone (*α-phenyl-β-methylbutane-αγ-dione*),

$$COPh\cdot CHMe\cdot COMe,$$

b. p. 150—152°/20 mm., is an almost colourless liquid, which does not solidify in a freezing mixture. Ferric chloride imparts a blue coloration to its solution in alcohol, which becomes more intense on standing. The freshly prepared alcoholic solution contains 6·4% of the substance in the enolic form, whilst a 1% solution in alcohol, after establishment of equilibrium, has 9% of the substance in this state, a similar solution in hexane having 11%. Addition of copper acetate to an alcoholic solution of methylbenzoylacetone causes the gradual precipitation of a green, crystalline *copper* salt, $(C_{11}H_{11}O_2)_2Cu$, m. p. 230°.

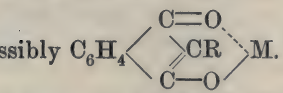
γ-Benzoyl-Δ^β-buten-β-ol, $COPh\cdot CMe{:}CMe\cdot OH$, m. p. 45—50°, is formed by the cautious acidification of a methyl-alcoholic solution of sodiomethylbenzoylacetone. When freshly prepared it contains 97% of the enolic form, gives an immediate precipitate with copper acetate, and an intense blue coloration with ferric chloride. It gradually passes into the oily equilibrium mixture, the velocity of change being

greatly increased by addition of traces of alkaline reagents, such as piperidine.

Ethylbenzoylacetone (*α-phenyl-β-ethylbutanedione*), b. p. 155—157°/20 mm., strongly resembles the above methyl compound. In the free state, about 3% of the enolic modification is present, whilst in 1% solution in ethyl alcohol or hexane, the corresponding figures are 7% and 9% respectively. The *copper* salt, $(C_{12}H_{13}O_2)_2Cu$, is a microcrystalline, greyish-green powder, m. p. 220°.

γ-Benzoyl-Δ^{β}-penten-β-ol has m. p. 32°. H. W.

Keto-enolic Isomerism of Indandione and Oxindone Derivatives. ARTHUR HANTZSCH (*Annalen*, 1912, **392**, 286—301. Compare following abstracts).—Colourless, or at most yellowish, diketones of the type of 2-alkylindandiones form intensely coloured metallic derivatives, which are formulated as oxindone derivatives, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{C(OM)}>CR$, or possibly



A chemical proof of enolisation during salt-formation is afforded by the facts of (i) the occasional isolation of coloured, labile-free enols (oxindones) and also of the colourless or yellowish, isomeric ketones (indandiones), and (ii) the occasional existence of coloured *O*-ethers (oxindone ethers) together with the colourless, isomeric alkylindandiones. An optical proof of the enolisation during salt-formation is furnished by the spectrometric method. The absorption spectra of the constitutively unchangeable 2 : 2-dialkylindandiones exhibit only general absorption, which is affected only slightly by the nature of the solvent or of the substituents. The enolic salts and ethers of 2-alkylindandiones show strong selective absorption, independent of the nature of the solvent.

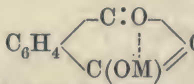
Enolisible indandiones are, like ethyl acetoacetate, extraordinarily optically variable according to the nature of the solvent and of the substituent. Thus 2-phenylindandione is colourless in ether and chloroform, but forms orange-red solutions in alcohols and deep red solutions in alkalis; the colourless solutions show only general absorption, whilst the coloured solutions exhibit selective absorption which is stronger the more intense is the colour. The coloured solutions are equilibrium mixtures of the keto- and the enolic modifications. Corresponding with this, it is found that 2-phenylindandione has a variable molecular refraction in different solvents, and exhibits an abnormally high exaltation during salt-formation.

The reasons for ascribing constitutions containing the 6-ring, $\cdot CR<\genfrac{}{}{0pt}{}{\dot{C}\cdot O}{\underset{\cdot}{C}\cdot O}>M$, to the metallic oxindone derivatives are, in the main, similar to those quoted in the case of conjugated *aci*-nitro-compounds (Hantzsch and Voigt, this vol., i, 151).

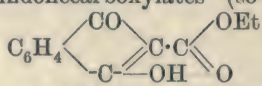
Two classes of coloured, metallic oxindone derivatives have been obtained. Metallic derivatives of 2-alkyl- or aryl-oxindones are red, and exhibit pronounced selective absorption with persistent bands. Metallic derivatives of oxindones containing a carbonyl group in

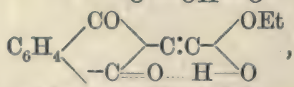
the side-chain, for example, 2-acetyloxindone, are yellow, and exhibit feebler selective absorption and shallow bands. Both classes of salts are conjugated oxindone derivatives, but contain different 6-rings; the red salts contain that given above, whilst the yellow salts are formulated thus: $\begin{array}{l}CO—C\cdot CR \\ | \quad\quad \| \\ C_6H_4\cdot C\cdot OM\end{array}\!\!>O.$ C. S.

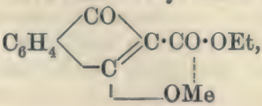
Simple Indandione and Oxindone Derivatives. ARTHUR HANTZSCH and FRITZ GAJEWSKI (*Annalen*, 1912, **392**, 302—318).—The following constitutively unchangeable indandiones have been prepared. 2-*Chloro-2-methylindandione*, $C_6H_4<{CO \atop CO}>CClMe$, m. p. 79°, colourless leaflets, from chlorine and aqueous sodiomethyloxindone; 2-*iodo-2-methylindandione*, m. p. 125°, pale yellow needles decomposed by light, prepared in a similar manner; 2-*benzoyl-2-methylindandione*, m. p. 127—128°, colourless crystals, from sodiomethyloxindone and benzoyl chloride in chloroform on the water-bath. The ketonic nature of the last substance is shown, not only by its general absorption, but also by its behaviour with alkalis, whereby a complex decomposition ensues, not a simple formation of benzoic acid and an oxindone derivative as in the case of phenyloxindone benzoate. 2-Phenylindandione and its chloro- and bromo-derivatives, which have been described as yellow, are obtained in colourless crystals from benzene.

All conjugated oxindone salts,  where R is an alkyl or aryl group, are deep red, never yellow; by interaction with alkyl haloids, they yield, not coloured *O*-ethers (compare following abstract), but disubstituted indandiones. However, 2-phenyloxindone salts and benzoyl chloride yield 2-*phenyloxindone benzoate*,

$$C_6H_4<{—CO— \atop C(OBz)}>CPh,$$

an orange-red substance which yields benzoic acid and the potassium derivative of 2-phenyloxindone by hydrolysis with alcoholic potassium hydroxide. Ethyl oxindonecarboxylates (so-called ethyl diketo-hydrindenecarboxylates),  or



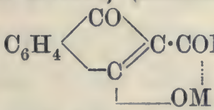
are intensely yellow, and, as enolic substances, react readily with bromine. Their metallic derivatives are always yellow. The sodium, *potassium*, *rubidium*, *caesium*, *ammonium*, *lithium*, *barium*, *strontium*, *calcium*, and *silver* derivatives of the preceding ester are described. The last derivative and methyl iodide at 0° yield *ethyl 3-methoxyindone-2-carboxylate*,  m. p. 38—41°, yellow crystals,

together with the stable, colourless, isomeric ethyl 2-methylindandione-2-carboxylate. The former is not changed to the latter by heating, but yields indandione at 100°. The preceding silver salt and benzoyl chloride in boiling benzene yield *ethyl 3-benzoyloxindone-2-carboxylate*, $C_6H_4<\genfrac{}{}{0pt}{}{—CO—}{C(OBz)}\gg C\cdot CO_2Et$, m. p. 146—148°, orange crystals, which yields benzoic acid and indandione by warming with sodium hydroxide.

Ethyl sodio-oxindone-2-carboxylate and aqueous mercuric chloride yield *ethyl indandione-2-carboxylate-2-mercurichloride*,

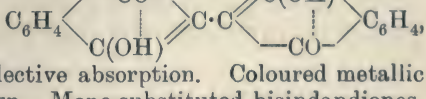
$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C(CO_2Et)\cdot HgCl,$$

m. p. 240—245°, colourless prisms.

2-Acetylindandione, which is best obtained by condensing together ethyl phthalate and acetone by means of sodium, is faintly yellow, and exhibits practically only general absorption in indifferent solvents. In the solid state, therefore, it is a triketone. However, in aqueous-alcoholic solution it is yellow, instantly decolorises bromine, and exhibits strong absorption; in this solvent, therefore, it is partly enolised. The metallic derivatives,  are yellow, and are not hydrolysed by alkalis; the *sodium, potassium, rubidium, caesium, lithium, calcium, strontium, barium, silver*, and *thallium* salts are described. The *mercurichloride*, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>CAc\cdot HgCl$, is colourless and microcrystalline.

Optically, real indandiones differ from the enolised oxindone derivatives by exhibiting general instead of selective absorption.

The molecular refraction, $M_D^{20°}$, of the constitutively unchangeable 2-phenyl-2-methylindandione is 70·40 and 70·90 in benzene and acetone respectively, whereas 2-phenylindandione, which is enolisible, has the values 65·25 and 67·42 respectively in the same two solvents; the exalted molecular refraction of 2-phenylindandione in acetone is a sign that the substance has partly enolised to the phenyloxindone in this solvent. A still greater exaltation is shown by the sodium derivative in acetone. C. S.

Bisindandione and Bisoxindone Derivatives. ARTHUR HANTZSCH and JOSEPH LISTER (*Annalen*, 1912, **392**, 319—322).—Corresponding with the structure, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>CH\cdot CH<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4$, ascribed to it by Gabriel and Leupold, bisindandione is colourless, and exhibits general absorption. There also exists, however, the isomeric enolic modification, bisoxindone,  which is brown, and exhibits selective absorption. Coloured metallic derivatives of the latter are known. Mono-substituted bisindandiones, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>CR\cdot CH<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4$, are colourless, and these have the

ketonic structure; they are enolised by alkalis, and thus yield metallic indandione-oxindone derivatives,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CR\cdot C\lessdot\begin{matrix}-CO-\\C(OM)\end{matrix}>C_6H_4.$$

Dimethylbisindandione, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CMe\cdot CMe<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$, which is best prepared from the thallium salt and methyl iodide at 100°, is colourless and exhibits general absorption.

Bisindandione forms a reddish-brown *thallium* derivative, dark red *barium* and *calcium* derivatives, and a blue *lead* derivative. The *mercury* derivative is colourless, and therefore has the ketonic structure; by acidifying its solution in acetone, it yields the brown bisoxindone, not the colourless bisindandione. C. S.

Bindone and *aci*-Bindone Derivatives. ARTHUR HANTZSCH and J. ZORTMAN (*Annalen*, 1912, **392**, 322—327).—The authors prefer the formula $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CH\cdot C\lessdot\begin{matrix}CH-\\C_6H_4\end{matrix}>CO$ to Hoyer's formula, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C:C<\begin{matrix}CH_2\\C_6H_4\end{matrix}>CO$, of bindone (anhydroindandione), because the former expresses clearly the great chemical analogy between bindone and enolisible indandiones containing the group

$$\cdot CO\cdot CHR\cdot CO\cdot.$$

A complete optical comparison is possible between bindone, its metallic derivatives, and its isomeric alkyl derivatives, because both forms of the latter, namely, the red *O*-ethers and the hitherto unknown yellow *C*-ethers, are stable. Like 2-phenylindandione, bindone can be obtained in the form of a dark violet, amorphous aci-*bindone* by acidifying its violet salt solutions in the cold; the *aci*-compound, however, changes very rapidly to ordinary yellow bindone. An equilibrium mixture of the two forms must exist in alcoholic and in aqueous alcoholic solutions, since yellow bindone dissolves in these solvents with a violet-red colour. Of the *O*-ethers described by Hoyer, the methyl ether has m. p. 213°, not 196°, and the ethyl ether has m. p. 164—165°, not 159°. The *benzoyl* derivative, m. p. 211—214°, is a dark red substance. Solutions of these three compounds are converted by alcoholic potassium hydroxide into violet solutions of the *aci*-bindone salt.

C-*Methylbindone*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CH\cdot C\lessdot\begin{matrix}CMe\\C_6H_4\end{matrix}>CO$, m. p. 174°, yellow crystals, is obtained by heating bindone with methyl iodide and methyl alcoholic sodium methoxide for many hours; its alkaline solution is red, like those of the *aci*-bindone ethers.

The absorption spectrum of bindone shows a band in the ultraviolet. *aci*-Bindone salts and ethers are optically very similar, and show selective absorption in the visible region of the spectrum.

C. S.

Tris- and Hydroxytris-indandiones. ARTHUR HANTZSCH and WALDEMAR FISCHER (*Annalen*, 1912, **392**, 328—347).—The formula of trisindandione stated by Liebermann and Flatow does not satis-

factorily explain why only a hydroxytrisindandione is obtained by oxidation. Moreover, trisindandione is easily converted by aqueous alkalis in the absence of air into two colourless carboxylic acids, from the alcoholic solution of which are obtained the *alcoholate*, m. p. 85—87°, of *indandionebisacetophenone*-oo′-*dicarboxylic acid*,

$$C_6H_4<\substack{CO\\CO}>C(CH_2\cdot CO\cdot C_6H_4\cdot CO_2H)_2,EtOH$$

(the *acid* itself has m. p. 145—147°), and *bisindandioneacetophenone-o-carboxylic acid*, $C_6H_4<\substack{CO\\CO}>C(CH_2\cdot CO\cdot C_6H_4\cdot CO_2H)<\substack{CO\\CO}>C_6H_4$, m. p. 178°, colourless needles. A solution of these two acids reddens in the air and then contains hydroxytrisindandione. A solution of the two acids in concentrated sulphuric acid yields trisindandione by dilution with water.

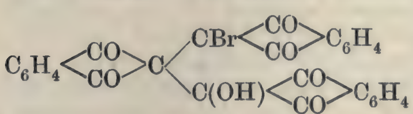
Liebermann and Flatow's formula, however, explains satisfactorily the following behaviour of trisindandione and its derivatives.

Pure sodium and potassium derivatives of trisindandione cannot be isolated, because of their rapid oxidation to salts of hydroxytrisindandione. The stable, orange-yellow *di-ammonium* derivative,

$$C_6H_4<\substack{CO\\CO}>C\left(C<\substack{C(ONH_4)\\C{=}O}>C_6H_4\right)_2,$$

however, is obtained by passing a mixture of dry oxygen and ammonia over trisindandione.

The almost colourless modification of hydroxytrisindandione is the ketonic form. The red *aci*-compound, which is best obtained by repeatedly digesting the ketonic form with a mixture of alcohol and acetone, has m. p. about 190°, not 218—219° (decomp.), as stated in the literature. The two forms, real acid and ψ-acid, cannot be distinguished by the gaseous ammonia test, because both yield ammonium salts with equal rapidity. They react differently, however, with bromine. The ketonic modification in glacial acetic acid yields *bromohydroxytrisindandione* (annexed formula), m. p. 182°, almost colourless needles, whilst the *aci*-compound in carbon disulphide yields hypobromous acid and



bromotrisindandione, $C_{27}H_{13}O_6Br$, m. p. 152° (decomp.). *Dibromotrisindandione*, $C_{27}H_{12}O_6Br_2$, m. p. 216°, colourless, microscopic prisms, is obtained from trisindandione and bromine containing a trace of iodine.

The dark red *potassium* derivative, $C_{27}H_{13}O_7K$, and *di-ammonium* derivative, $C_{27}H_{12}O_7(NH_4)_2$, of hydroxytrisindandione are described. Their constitutions correspond with that of *aci*-hydroxytrisindandione itself. In water or alcohol, however, these salts form orange *hydrates* or *alcoholates*, $C_{27}H_{13}O_7K,2EtOH$ and $C_{27}H_{12}O_7(NH_4)_2,2EtOH$, in which probably the hydroxylated indandione ring has been ruptured.

aci-*Hydroxytrisindandione diethyl ether*, $C_{27}H_{12}O_7Et_2$, m. p. 193—195°, a red substance, can only be prepared by treating the silver salt with ethyl iodide in darkness.

The absorption spectra of *aci*-hydroxytrisindandione, its potassium derivative, and its diethyl ether are identical. This furnishes another

proof of the statement that colour and absorption are unchanged if the constitution of an acid does not alter during its conversion into its salts or esters. The absorption spectra of the dimetallic derivatives of hydroxytrisindandione differ somewhat from those of the monometallic salts in alcohol, an explanation of which has been given above.

C. S.

Transformation of Pyrogallol Triacetate. GUSTAV HELLER and OTTO FRITSCH (*Ber.*, 1912, **45**, 2389—2392. Compare this vol., i, 274).—By heating for two hours at 145—147° with its own weight of zinc chloride, pyrogallol triacetate loses one acetyl group; the other two migrate into the nucleus, and gallodiacetophenone is produced. By benzoylation in pyridine, the latter yields *tribenzoylgallodiacetophenone*, $C_{31}H_{22}O_8$, m. p. 189°.

By heating with zinc chloride at 130—135° for one hour, pyrogallol triacetate is converted into *gallacetophenone diacetate*, m. p. 217—219°.

C. S.

Oxidation of Anilinoquinones to Benzidine Derivatives. KURT BRASS (*Ber.*, 1912, **45**, 2529—2533).—As in an earlier investigation (Pummerer and Brass, Abstr., 1911, i, 654) only one molecule of α-naphthaquinone could be made to condense with benzidine, the author has attempted to prepare indirectly a substance which structurally shall be the symmetrical condensation product of two molecules of α-naphthaquinone with one molecule of benzidine.

If 2-anilino-α-naphthaquinone is oxidised by manganese dioxide in concentrated sulphuric acid, the resultant liquid on pouring on to ice deposits dark brown flocks of N : N′-*bis-α-naphthaquinonyl*-2-*benzidine*, $C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot C_{10}H_5O_2$.

The structure attributed to this substance is confirmed by the formation of benzidine on fusion with potassium hydroxide, and by the oxidation of 3-chloro-2-anilino-α-naphthaquinone in an analogous manner to N : N′-*bis-3-chloro-α-naphthaquinonyl*-2-*benzidine*,

$$C_{10}H_4O_2Cl\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot C_{10}H_4O_2Cl,$$

red needles and prisms, m. p. 325° (decomp.); this substance dissolves in concentrated sulphuric acid with an intense bluish-violet colour; it is reduced by hyposulphite to a yellow vat, which dyes cotton a fast reddish-violet; on fusion with potassium hydroxide, it yields benzidine.

That in the formation of the above substances coupling occurs at the para-position is indicated by the failure to obtain any such oxidation product from 2-*p*-toluidino-α-naphthaquinone. D. F. T.

Preparation of Anthracene Derivatives. JACOB MEYER (D.R.-P. 247187).—When ketones of the general formula $R\cdot CO\cdot CH_3$ (where R is an aliphatic, aromatic, or mixed residue) are heated at 120—130° during about an hour with anthraquinone derivatives in concentrated sulphuric acid solution, characteristic fluorescent condensation products are formed.

Anthraquinone (100 parts) acetone (50—60 parts) in 2000 parts of concentrated sulphuric acid furnishes a *compound*, orange-yellow

crystals, m. p. 252°, which crystallises from xylene and dissolves in concentrated sulphuric acid with a red fluorescence; when the anthraquinone is replaced by β-methylanthraquinone, the *product* has similar properties.

The *compounds* from acetone and α- or β-chloroanthraquinone are crystalline, orange powders, and decompose indefinitely when heated, whilst α- and β-aminoanthraquinones yield orange-red and orange-yellow powders respectively, the former exhibiting yellowish-brown and the latter brick-red fluorescence in concentrated sulphuric acid, and are distinct from those previously obtained by similar condensations in alkaline solution.

A *compound*, greenish-yellow needles, m. p. 333°, is obtained from anthraquinone and acetophenone, whilst the same with *m*-nitroacetophenone forms pale brown needles. F. M. G. M.

Reduction of Some Hydroxyanthraquinones. YASUSABRO HIROSÉ (*Ber.*, 1912, 45, 2474—2480).—An attempt has been made to characterise more fully the reduction products of some hydroxyanthraquinones, using, in addition to the ordinary elementary analysis and determination of molecular weight, Zerewitinoff's method of determining free hydroxyl groups and the method of determining acetic acid in the acetyl derivatives.

Anthrachrysone yields on reduction a product crystallising in yellowish-white, microscopic needles, m. p. 245°, which corresponds with either a penta-acetoxyanthracene or a tetra-acetoxy-anthranol or -anthrone.

Trimethylanthrachrysone forms yellow needles, m. p. 225°, and yields an *acetyl* derivative, crystallising also in yellow needles, m. p. 220°.

Triacetyltrimethyldihydroanthrachrysone, formed on reduction, separates in pale yellow needles, m. p. 241°; it is shown to contain three methyl and three acetyl groups, and a residue, $C_{17}H_{16}O_6$.

Quinalizarin is reduced by tin, acetic and hydrochloric acids to the oxanthranol stage, $C_6H_2(OH)_2{<}{\begin{smallmatrix}-CO-\\CH(OH)\end{smallmatrix}}{>}C_6H_2(OH)_2$, the product crystallising in orange-yellow needles, m. p. 245°. The *tetra-acetyl* derivative forms pale yellow needles, m. p. 215°, which exhibit a blue fluorescence in solution. On repetition, the tetra- or penta-acetyl derivative of a compound with an oxygen atom less is obtained.

Anthrarufin is reduced to the hydranthone stage,

$$OH\cdot C_6H_3{<}{\begin{smallmatrix}CO-\\CH_2\end{smallmatrix}}{>}C_6H_3\cdot OH.$$

Using acetic anhydride, sodium acetate, and zinc dust to effect reduction, a *triacetylated anthranol* of anthrarufin is obtained in colourless needles, m. p. 248—255°.

When diacetylanthrarufin is reduced, the process stops at the dianthranol stage, $OAc\cdot C_6H_3{<}{\begin{smallmatrix}C(OH)\\|\\C(OAc)\end{smallmatrix}}{>}C_6H_3\cdot OAc$; the product forms almost colourless platelets, m. p. 265—270°, which fluoresce strongly in solution.

Chrysazin is reduced to the anthranol stage,

$$OH\cdot C_6H_3{<}{\begin{smallmatrix}CH-\\|\\C(OH)\end{smallmatrix}}{>}C_6H_3\cdot OH,$$

the compound crystallising in yellow plates, m. p. 180°. Using acetic anhydride, the same product is obtained from chrysazin or its diacetyl derivative, namely: $OAc\cdot C_6H_3<\begin{matrix}CO\\CH(OH)\end{matrix}>C_6H_3\cdot OAc$, m. p. 188—190°. E. F. A.

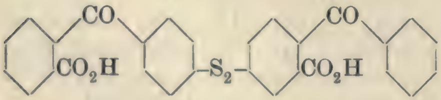
Metallic Salt Precipitates of Dyes Containing Hydroxyl Groups. P. BRUNO GUGGIARI (*Ber.*, 1912, **45**, 2442—2447).—The composition of the metallic salt precipitates obtained with alizarin, β-nitroalizarin, quinizarin, naphthazarin, carminic acid, and anthragallol has been determined. The tendency is to form the normal salt, that is, that in which the acid groups of the dye are completely saturated by the basic groups of the metallic hydroxide. Difficulties are introduced by the retention of impurities in the flocculent precipitates.

The quinizarin precipitates have the same composition as those given by alizarin, but the former are much more sensitive towards weak acids, a few drops of acetic acid preventing precipitation.

E. F. A.

Preparation of Anthraquinone Derivatives Containing Sulphur. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 247412).—Mercaptans of the anthraquinone series have been previously prepared from rhodanthraquinones, chloroanthraquinones, or anthraquinonesulphonic derivatives. It is now found that they can be readily obtained in satisfactory yield from halogenated *o*-benzoylbenzoic acids or from diazo-*o*-benzoylbenzoic acids by condensation and subsequent reduction.

Sodium 4′-chloro-*o*-benzoylbenzoate (225 parts) is heated (with continual stirring) at 170° during four hours with a solution of sodium hydrogen sulphide (134 parts NaSH), and the *4′-thiol-o-benzoylbenzoic acid*, after purification by several solutions in alkali, isolated as a pale yellow or colourless powder; this acid when oxidised in alkaline solution furnishes *o-benzoylbenzoic acid 4′-disulphide* (annexed formula) as a pale yellow powder.



When the foregoing disulphide is heated at 150° during one and a-half hours with 10 parts of concentrated sulphuric acid, condensation occurs, yielding anthraquinone-2 : 2′-disulphide, and this when boiled with aqueous alkaline sodium sulphide furnishes β-thiolanthraquinone (Abstr., 1909, i, 496). F. M. G. M.

Autoxidation of Phenanthraquinone in the Presence of Aromatic Hydrocarbons. ALFRED BENRATH and ALEXANDER VON MEYER (*Ber.*, 1912, **45**, 2707—2708. Compare Klinger, Abstr., 1911, i, 633).—When phenanthraquinone suspended in toluene, or *o*-, *m*-, or *p*-xylene, is exposed to the action of light, diphenic acid is obtained, together with benzoic acid or the corresponding toluic acid. No phthalic acid could be detected. Oxidation occurs most rapidly

with the methyl derivatives of benzene, more slowly with ethylbenzene, still more slowly with cumene, whilst no oxidation could be detected in the presence of benzene. Aldehydes appear to be formed in small amount during the reactions.

Since phenanthraquinone does not appear to undergo change when exposed to the action of air and water, the authors are led to the conclusion that the hydrocarbons unite with phenanthraquinone, and that the quinol ethers so obtained suffer oxidation. H. W.

[Preparation of Phenanthrene Derivatives Containing Sulphur.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 247415).—When nitrophenanthraquinones or their derivatives are heated with sulphur and an alkali sulphide, either with or without a diluting agent, they yield compounds which dye vegetable fibre a fast yellow to brown tone.

One hundred parts of 2 : 7-dinitrophenanthraquinone, m. p. 300° (Abstr., 1902, i, 797; 1904, i, 70), was heated at 180—220° with sulphur (200 parts), sodium sulphide crystals (300 parts), and water (500 parts) during eight to ten hours; the *product*, a black powder, is insoluble in water, acids, or alkalis, but soluble in sodium sulphide.

The analogous *compounds* from the isomeric 2 : 7-dinitrophenanthraquinone, m. p. 215—217° (*loc. cit.*), from 4 : 5-dinitrophenanthraquinone, and from *dibromodinitrophenanthraquinone*, m. p. above 300° (obtained by nitrating dibromophenanthraquinone, m. p. 284°), are also described in the original. F. M. G. M.

Preparation of Cyanoaminoformyl Esters. EMANUEL MERCK (D.R.-P. 247453).—Ethyl cyanoaminoformate has previously been prepared in ethereal solution (Abstr., 1878, ii, 214); the reaction is now found to take place in aqueous alkaline solution with an ester of chloroformic acid and cyanamide:

$$Cl\cdot CO_2R + NH_2\cdot CN = CO_2R\cdot NH\cdot CN + HCl.$$

Menthyl cyanoaminoformate is obtained as an oil from menthylchloroformate and cyanamide; its *silver* salt forms microscopic needles, and the *sodium* salt, hygroscopic needles; the *guaiacyl* ester (from guaiacyl chloroformate) is a colourless oil; its *silver* and *sodium* salts form needles.

Oxycamphor cyanoaminoformate, colourless needles, m. p. 112° (indefinite), is prepared from oxycamphorchloroformate and cyanamide; its *silver* salt forms colourless aggregates; the *sodium* salt, needles, has m. p. 141°, or (after drying at 100°) decomposes at 260°.

F. M. G. M.

Preparation of Allophanic Acid Esters. EMANUEL MERCK (D.R.-P. 248164. Compare preceding abstract).—When cyanoaminoformyl esters are boiled with dilute mineral acids, they yield allophanic esters: $CO_2R\cdot NH\cdot CN + H_2O = CO_2R\cdot NH\cdot CO\cdot NH_2$; by this means ethyl cyanoaminoformate is converted into ethyl allophanate; *guaiacyl allophanate*, colourless prisms, decomp. 176°, is obtained from guaiacyl cyanoaminoformate with 20% hydrochloric acid. *Oxycamphor allophanate*, colourless needles, m. p. 204°, is prepared in 50% sulphuric acid solution at 60—70°; *menthyl allophanate*, colourless needles, has

m. p. 215°. *Methyl salicylallophanate*, colourless needles, decomp. 175°, is obtained by treating cyanamide with methyl salicylchloroformate (Abstr., 1901, i, 697) in aqueous solution, and subsequently boiling with an acid. F. M. G. M.

Terpenes and Ethereal Oils. CXI. OTTO WALLACH (*Annalen*, 1912, 392, 49—75).—Pulegenolide is not inactive, as has hitherto been supposed, but has a very feeble rotatory power. Dihydropulegenolide, obtained by its reduction by Paal's method (Abstr., 1911, i, 469), has $[\alpha]_D$ $-56\cdot85°$ in methyl alcohol.

The reduction of *dl*-carvenolide by hydrogen and colloidal palladium in methyl alcohol yields *dl*-dihydrocarvenolide, which is proved to be identical with dihydropulegenolide by its m. p., 50—51°, and rotatory power, $[\alpha]_D^{18}$ $-57\cdot57°$, and by the fact that both lactones yield the same hydroxy-acid. From this it follows that both have probably the constitution $CH_2<\begin{matrix} CHMe\cdot CH\cdot CO— \\ CH_2—CH\cdot CMe_2 \end{matrix}>O$, and whether this is correct or not, that pulegenolide and carvenolide are unsaturated compounds differing only in the position of the double linking.

The presence of a 5-ring in pulegenolide (or in its generator, pulegenic acid) has been established beyond doubt. Hence a change of a 6-ring to a 5-ring must have occurred during the conversion of tribromocarvone into carvenolide. The readily fusible by-product obtained during the reduction of pulegenolide (*loc. cit.*) is probably only impure dihydropulegenolide (dihydrocarvenolide).

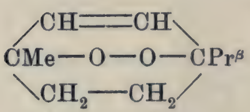
By fusion with potassium hydroxide, *i*-carvenolic acid yields an acid, $C_7H_{10}O_2$, m. p. 130°, which is very probably 1-*methyl*-Δ^1-cyclo*penten*-2-*carboxylic acid*, $\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CMe \end{matrix}>C\cdot CO_2H$. By hydrolysis with boiling potassium hydroxide, *i*-dihydrocarvenolide yields i-*dihydrocarvenolic aci* , $C_{10}H_{18}O_3$, m. p. 87—88°, and *dl*-dihydrocarvenolide (dihydropulegenolide) yields dd-*dihydrocarvenolic acid*, $C_{10}H_{18}O_3$, m. p. 87—88°, $[\alpha]_D^{17}$ $+9\cdot43°$. By slow, dry distillation, *i*-dihydrocarvenolic acid yields a *hydrocarbon*, C_9H_{16}, b. p. 135° (*nitrosochloride*, m. p. 104—105°, needles; *nitrolpiperidide*, m. p. 110—111°), and an *acid* (*silver* salt, $C_{10}H_{15}O_2Ag$), which resembles pulegenic acid.

The reduction of *d*-pulegenamide in aqueous methyl alcohol by hydrogen and colloidal palladium proceeds with difficulty (probably on account of the presence of a semicyclic linking) and yields d-*dihydropulegenamide*, $C_{10}H_{19}ON$, m. p. 150°, $[\alpha]_D^{20}$ $+4\cdot487°$, by the hydrolysis of which a liquid dihydropulegenic acid is obtained.

[With ERWIN MEYER.]—Pulegene is not reduced satisfactorily by Paal's process, but is so by Skita's modification thereof, yielding *dihydropulegene* (1-*methyl*-3-iso*propyl*cyclo*pentane*), C_9H_{18}, b. p. 142—144°, D^{22} 0·7730, n_D 1·4236.

By reduction by Paal's method, ascaridole (Abstr., 1908, i, 667) rapidly absorbs four atoms of hydrogen and yields two products. The main product, which is only slightly volatile with steam, is a new 1 : 4-*terpin*, $OH\cdot CMe<\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}>CPr^\beta\cdot OH$, m. p. 116—117°, large,

glistening prisms. It is optically inactive, yields compounds of the terpinene series by treatment with hydrogen haloids, and is converted by warming with oxalic acid into 1 : 4-cineole (Abstr., 1907, i, 943) and a small quantity of an unsaturated *alcohol*. The latter could not be isolated in a pure state, but is proved to be Δ^3-menthen-1-ol by oxidation by 1% potassium permanganate at 0°, whereby is obtained 1 : 3 : 4-trihydroxymenthane, which is converted by warm dilute sulphuric acid into *p*-cymene and Δ^1-menthen-3-one. All these facts prove that the 1 : 4-terpin is a compound of the terpinene series. The second product of the reduction of ascaridole is an oil which is easily volatile with steam, and is a mixture of saturated and unsaturated substances. By further treatment with hydrogen and palladium, and subsequent removal of the still unsaturated impurities by potassium permanganate, the oil yields a substance, $C_{10}H_{19}\cdot OH$, b. p. 207—208°, D^{19} 0·9080, n_D 1·4656, which is converted by zinc chloride into a *hydrocarbon*, $C_{10}H_{18}$, b. p. 173·5—175·5°, D^{19} 0·821, n_D^{19} 1·4558 ; this hydrocarbon is probably a mixture of menthenes. The preceding facts are in harmony with the annexed formula of ascaridole, not with that proposed by Nelson (Abstr., 1911, i, 797).



[With Hans Schlubach.]—1-Methyl-5-*iso*propyl-Δ^6-*cyclo*hexen-2-one (*iso*camphor) and its reduction product have constitutions quite different from those previously ascribed to them (Abstr., 1911, i, 312) and indicated by the preceding name. It is now shown that the reduction product, which is easily obtained from *iso*camphor by Paal's method, is not 1-methyl-5-*iso*propyl*cyclo*hexan-2-one, but is identical with dihydropinolone (3-acetyl*iso*propyl*cyclo*pentane) (Abstr., 1911, i, 891). *iso*Camphor is certainly not identical with pinolone. The proof of the presence of a 5-ring in *iso*camphor is as follows. *iso*Camphoroxime in alcoholic solution is reduced by Paal's method (which excludes the possibility of any intramolecular change), and the products, after acidification with sulphuric acid and distillation with steam, are dihydropinolone and dihydropinolylamine (identical with the base obtained by the reduction of dihydropinoloneoxime by sodium and alcohol). Possibly *iso*camphor is an active modification of 3-acetyl*iso*propyl-Δ^2-*cyclo*pentene (*loc. cit.*) ; an explanation is, as yet, not possible of the series of changes whereby the 5-ring is produced during the formation of *iso*camphor from fenchoneoxime or camphoroxime through the nitro-imines. C. S.

Pinene Hydriodide. (3-Iodocamphane) and Camphane. Ossian Aschan (*Ber.*, 1912, **45**, 2395—2398).—The interaction of magnesium iodide and pinene hydrochloride for two hours in boiling ether and subsequently, after removal of the solvent, for three hours on the water-bath, leads to the formation of pinene hydriodide, camphane and bornylene being obtained as by-products.

Pinene hydriodide and moist silver oxide, shaken for a long time with alcohol at about 50°, yield a *substance*, $C_{10}H_{18}O$, b. p. 207—211°, which is unsaturated, does not react with semicarbazide, and is apparently a new terpene alcohol.

Camphane is readily obtained from pinene hydriodide by treatment with 12% hydrogen chloride in glacial acetic acid and zinc dust.

The conversion of camphane into derivatives of camphor by passage through a dog is mentioned. C. S.

[Essential Oils.] ROURE-BERTRAND FILS (*Sci. Ind. Bull.*, 1912, [iii], 1, 3—160).—[JUSTIN DUPONT and LOUIS LABAUNE.]—A method for the estimation of geraniol in citronella oil is described, based on the fact that on treatment with hydroxylamine the citronellal is converted into the oxime, and that on further treatment with acetic anhydride the oxime is dehydrated, giving the corresponding nitrile, whilst the geraniol and other alcohols are acetylated. The quantity of esters thus formed can then be estimated in the usual way by hydrolysis with standard alkali. The results obtained by experiments on Java citronella oil indicate that the latter contains one or more alcohols of higher boiling point than geraniol; the new constituents *iso*amyl alcohol and *iso*valeraldehyde have also been noted in this oil.

Cupressus lusitanica branches gave 0·25% of bright yellow oil, D^{15} 0·8723, $a_D + 9°10'$, acid value 1·05, saponification value 9·8, soluble in 3 or more vols. of 90% alcohol.

C. sempervirens fastigiata branches gave 0·20% of brown oil, D^{15} 0·8744, a_D + 12°6′, acid value 0·7, saponification value 4·9, soluble in 3·5 or more vols. of 90% alcohol. The fruits of the same plant, freed from seeds, gave 0·41% of amber-tinted oil, D^{15} 0·8739, a_D + 29°52′, acid value 1·0, saponification value 9·8, soluble in 4 or more vols. of 90% alcohol. The seeds yielded only a trace of essential oil.

The aerial portion of parsnip (*Pastinaca sativa*) grown in Piedmont gave 0·1 per cent. of reddish-brown oil, D^{15} 0·8970, a_D + 0°6′, acid value 5·6, saponification value 228·9, soluble in 2 or more vols. of 80% alcohol.

Wild celery oil from Algeria, distilled from the entire mature plant, had D^{15} 0·8467, a_D + 69°18′, acid value 0, saponification value 14·7, and was miscible with 95% alcohol, but gave cloudy solutions with weaker alcohol.

Wild carrot oil from Puy-de-Dôme, distilled from the entire mature plant, had D^{15} 0·9016, a_D − 6°56′, acid value 2·7, saponification value 195·4.

The "Bulletin" also contain a critical résumé of recent work on essential oils and their constituents. T. A. H.

[Essential Oils.] SCHIMMEL & Co. (*Bericht*, October, 1912, pp. 22—200).—A comparison has been made of the various methods available for the estimation of citronellal and gerianol in citronella oil, including that due to Dupont and Labaune (see preceding abstract). It is pointed out that these constituents should be separately estimated, and that for geraniol the phthalic anhydride process probably gives the best results, whilst for citronellal Dupont and Labaune's method is satisfactory, as is also Kleber's phenylhydrazine process. Boulez's method (this vol., ii, 1105) gives good results for citronellal in Ceylon citronella oil. In determining the so-called "total geraniol" of the oil by acetylation, sodium acetate should always be used.

Cymbopogon coloratus oil, from Fiji, is golden-yellow to brown, has D^{15} 0·9155—0·920, α_D $-7°43'$ to $-8°40'$, contains geraniol 15·6% and citronellal 45·7—49·5%, and is soluble in one or more volumes of 80% alcohol (compare *Bull. Imp. Inst.*, 1912, **10**, 27). *Cymbopogon sennaarensis* (*C. Jwarancusa*, Abstr., 1911, i, 476), herb from the Sudan, gave on distillation 1·005% of oil, D^{15} 0·9383, α_D^{20} $+34°14'$, containing 17·3% of alcohols and 26—27% of constituents combining with sodium hydrogen sulphite. The principal constituent is a ketone resembling pulegone, and a dextrorotatory terpene is also present (*Bull. Imp. Inst.*, 1912, **10**, 31).

The following new oils have been described by Baker and Smith (*J. Roy. Soc. N.S.W.*, 1911, **45**, 267). *Eucalyptus acaciaeformis* leaves yield 0·197% of brown oil, D^{15} 0·8864, α_D $+35·7°$, n_D^{20} 1·4713, containing *d*-pinene, a sesquiterpene, and geranyl acetate (?). *E. Andrewsi* leaves gave 1·27% of lemon-yellow oil, D^{15} 0·8646, α_D $-41·5°$, n_D^{15} 1·4854, ester number 4·3, containing *l*-phellandrene, piperitone, and a sesquiterpene. *E. campanulata* leaves gave 0·851% of bright yellow oil, D^{15} 0·8804, $[\alpha]_D$ $-25·8°$, n_D^{18} 1·4856, saponification number 7·6, containing phellandrene, cineole, piperitone, and eudesmol. *E. Bridgesiana* leaves gave 0·73 to 0·74% of oil, D^{15} 0·9223 to 0·9246, α_D $+1·8°$ to $+1·9°$, n_D^{20} 1·4716—1·4729, saponification number 7·6 to 8·7, containing 73—78% of cineole. *E. laevopinea* oil has D^{15} 0·8875, α_D $-30·7°$ to $-33·3°$, D^{19} 1·4691, and contains not more than 5% of cineole. *E. dextropinea* leaves gave 1·02% of oil, D^{15} 0·8831, α_D $+24·2°$, n_D^{21} 1·4688, saponification number 22·1, containing 3·7% of geranyl acetate. *E. nova-anglica* oil had D^{15} 0·9221 to 0·9301, α_D $+0·9°$ to $+5·8°$, n_D^{15} 1·4892—1·4944, n_D^{18} 1·4857, saponification number 5·7—6·9, which is rich in sesquiterpenes, but contains only small amounts of cineole and phellandrene.

Silver fir seeds (*Abies pectinata*) after being crushed yielded 12—13% of oil, D^{15} 0·8629—0·8668, α_D $-68°14'$ to $-76°38'$, n_D^{20} 1·47636 to 1·47812, acid number 0·5—1·8, ester number 0·9 to 3·7, soluble in 5—7 or more vols. of 90% alcohol.

"Lawang" bark from the Dutch East Indies, and probably derived from *Cinnamomum iners*, yields according to Mann (*Pharm. Journ.*, 1912, **89**, 145) 0·5% of an oil, $D^{15·5}$ 1·0104, α_D^{20} $-6·97°$, n_D^{20} 1·5095, acid number 1·15, ester number 41·87, saponification number after acetylation 121·9, having an odour recalling those of nutmeg, sassafras, and cloves.

The linalool oxide obtained from linaloe oil is now shown to be identical with that prepared by Prileschaéeff (Abstr., 1910, i, 86), both giving the same *phenylurethane*, m. p. 58·5—59°, crystallising in colourless prisms from alcohol. The oxide is probably formed by saturation of the end group $-CH{:}CH_2$ of linalool by one atom of oxygen.

Baker and Smith (*Proc. Roy. Soc. N.S.W.*, 1911, **45**, 365) have described the following oils from *Melaleuca* spp. of Australia: *M. genistifolia* leaves and twigs gave 0·526% of bright yellow oil, D^{15} 0·8807, α_D $+32·7°$, n_D^{20} 1·4702, saponification number 6·8, containing *d*-α-pinene (80 to 90%), cineole (2%), and a sesquiterpene. *M. gibbosa* leaves and twigs gave 0·158% of dark yellow oil,

D^{15} 0·9138, a_D +4·5°, n_D^{20} 1·4703, saponification number 9·9, containing cineole 61·5%. a-pinene, a sesquiterpene, and terpinyl acetate (?). *M. pauciflora* leaves and twigs gave 0·3% of a viscous, dark amber-tinted oil, D^{15} 0·9302, a_D +3·3°, n_D^{24} 1·4921, saponification number 8·25, containing cineole, 8·7%, terpinyl acetate (?), terpineol (?), limonene (?), and at least 67% of a sesquiterpene giving a red colour with acetic and sulphuric acids and a blue coloration with bromine vapour.

An authentic sample of larch turpentine was pale yellow in colour, viscous, and had a_D +29°20′, acid number 69·5, ester number 55·9, and was soluble in three parts of 80% alcohol. On steam-distillation it yielded 13·5% of larch turpentine oil, D^{15} 0·8649, a_D −8°15′, n_D^{20} 1·46924, acid number 0, ester number 5·9, and was soluble in six volumes or more of 90% alcohol. On fractionation it yielded 60% at 157—161°, 20% at 161—164°, and 6% at 164—168°.

Juniperus phoenicea oil, distilled in Cyprus from entire ground berries, had D^{15} 0·8688, a_D +3°4′, n_D^{20} 1·47210, acid number 0·6, ester number 10·2, and was soluble in eight or more volumes of 90% alcohol with slight opalescence.

A critical survey of recent literature on the chemistry of essential oils is also published. T. A. H.

The Constituents of Ethereal Oils (the Composition of Essential Oil of Vetiver). FRIEDRICH W. SEMMLER, FELIX RISSE, and FRITZ SCHRÖTER (*Ber.*, 1912, 45, 2347—2457. Compare Genvresse and Langlois, Abstr., 1903, i, 187).—Essential oil of vetiver was separated by fractional distillation under reduced pressure, and the fractions investigated chemically. A specimen obtained from a German firm showed marked differences in composition from oil distilled in Réunion, the variations being attributable to differences in the details of the method of extraction.

The highest fraction (b. p. 250—300°/12 mm.) from the German oil of vetiver contains an *ester* of a primary alcohol, *vetivenol*, $C_{15}H_{24}O$ (distinct from the vetivenol, $C_{15}H_{26}O$, of Genvresse and Langlois), b. p. 170—174°/13 mm., D^{20} 1·0209, n_D 1·52437, a_D +34·5°, with *vetivenic acid*, $C_{15}H_{22}O_2$, b. p. 202—205°/13 mm., *methyl* ester, b. p. 170—173°/18 mm., D^{20} 1·0372, n_D 1·50573, a_D +42·2°. Both the alcohol and the acid are tricyclic with one ethylenic linking, the former compound being reducible by hydrogen and platinum-black to *dihydrovetivenol*, b. p. 176—179°/17 mm., D^{20} 1·0055, n_D 1·51354, a_D +31°; *acetate*, b. p. 180—184°/19 mm., D^{20} 1·0218, n_D 1·50433, a_D +28·48°.

The above vetivenic acid is also present in the fraction b. p. 190—250°/12 mm., but in this case as an ester with a *bicyclic* primary alcohol, *vetivenol*, $C_{15}H_{24}O$, b. p. 168—170°/14 mm., which could not be obtained quite pure.

Two hydrocarbon fractions also were isolated, of composition $C_{15}H_{24}$ (vetivene), one apparently being a diolefinic bicyclic (b. p. 137—140°/16 mm.) and the other a mono-olefinic tricyclic compound (b. p. 123—130°/16 mm.).

In Réunion oil of vetiver, the ester of vetivenic acid with tricyclic

vetivenol is lacking, otherwise the constituents are the same as in the German sample; a portion of the tricyclic vetivenol separated was converted by phosphorus pentachloride into the *chloride*, $C_{15}H_{23}Cl$, b. p. 140—147°/10 mm., D^{20} 0·9679, n_D 1·52640, α_D −24°, which by reduction with sodium and alcohol gave an artificial vetivene, the product varying in properties with the experimental details.

No indication of the vetivenol, $C_{15}H_{26}O$, described by earlier investigators was observed. D. F. T.

Sterols from Castilloa- and Ficus-caoutchouc. A. J. Ultée (*Chem. Weekblad*, 1912, 9, 773—777).—*Castilloa*-caoutchouc contains about 20% of a resin, the alcoholic extract from which contains β-amyrin acetate, m. p. 233—234°; lupeol acetate, m. p. 213°; α-amyrin, m. p. 184—188°; and an acetate, m. p. 121—122·5°, probably identical with the compound obtained by Cohen from an African *Euphorbia*-rubber (Abstr., 1908, i, 884).

Ficus-caoutchouc yields a resin, from which alcohol extracts a *substance*, m. p. 76°, also obtained in small proportion from castilloa-caoutchouc. α-Amyrin acetate, m. p. 218°, is also present, but this rubber is comparatively deficient in sterols. A. J. W.

Resin Balsam of Pinus cambodgiana. Arthur Wichmann (*Arch. Pharm.*, 1912, 250, 472—477).—The resin balsam of *Pinus cambodgiana* is a yellowish-greyish-white substance of the consistence of honey. It has a pleasant, aromatic odour, and dries to an opaque resin by exposure to air in thin layers. It dissolves completely in the usual solvents except water, and has acid number 145·315 (direct) or 148·12 (indirect method). By distillation with steam, it yields a yellow, aromatic oil, D 0·892, n^{21} 1·48455, in 19·35% yield. By extracting the ethereal solution of the purified residue with 1% ammonium carbonate, *cambopinic acid*, $C_{11}H_{18}O_2$, is obtained. It is a colourless, odourless, tasteless, amorphous powder, m. p. 78°. The ethereal solution then yields to 1% sodium carbonate, *cambopinonic acid*, $C_{16}H_{24}O_2$, m. p. 71°, which resembles the preceding acid in physical characteristics. The ethereal solution then contains only *camboresen* in very small amount. C. S.

The Main Constituent of Japanese Lac. III. Catalytic Reduction of Urushiol. Rikō Majima (*Ber.*, 1912, 45, 2727—2730. Compare Abstr., 1907, i, 1032; 1909, i, 402, 915).—Previous investigations of urushiol have failed to yield crystallisable products. The application of Willstätter's method of catalytic reduction has led to the isolation of well-crystallised derivatives of urushiol, diacetyl- and dimethyl-urushiol, from the constitution of which the molecular formula, $C_{20}H_{30}O_2$, for urushiol itself is established. Reduction appears to take place exclusively in the side-chain.

Hydrourushiol, $C_{20}H_{34}O_2$, was obtained in good yield by the action of hydrogen on an alcoholic solution of purified urushiol in the presence of platinum. It crystallises in needles, m. p. 58—59°, mol. wt. (in benzene solution) 302. Crude urushiol, when similarly treated,

yielded 68% hydrourushiol and 32% of an amorphous black residue. *Dimethylhydrourushiol*, $C_{20}H_{32}(OCH_3)_2$, prisms, m. p. 36—37°, and *diacetylhydrourushiol*, m. p. 50—51°, were similarly obtained from dimethylurushiol and diacetylurushiol respectively.

[With TEPPEI OKADA.]—The catalytic reduction of elæostearic acid (Abstr., 1909, i, 204) gives an almost quantitative yield of stearic acid, thus confirming the normal linking of the carbon chain in this substance (compare Kametaka, Trans., 1903, **83**, 1042).

H. W.

Synthesis of Phenolic Glucosides. EMIL FISCHER and HERMANN STRAUSS (*Ber.*, 1912, **45**, 2467—2474).—On shaking an alkaline solution of phloroglucinol with an ethereal solution of acetobromoglucose and removal of the acetyl groups, phloroglucinol-*d*-glucoside is obtained, identical with the compound prepared by Cremer and Seuffert from phloridzin by heating it with barium hydroxide. In a similar manner resorcinol glucoside is obtained. Both compounds are hydrolysed by emulsin.

Acetobromoglucose readily couples with tribromophenol, but the acetyl groups can only be removed by liquid ammonia at the ordinary temperature, other alkalis bringing about complete decomposition.

Resorcinol-d-*glucoside* crystallises in colourless, short needles, which sinter at 185°, m. p. 190° (corr.), $[\alpha]_D^{24}$ $-70°$. It tastes bitter and is readily hydrolysed by boiling dilute mineral acids.

Phloroglucinol-d-*glucoside* crystallises in ray-like aggregates, m. p. 239° (corr.), $[\alpha]_D^{22}$ $-74°$. 2 : 4 : 6-*Tribromophenoltetra-acetyl*-d-*glucoside* crystallises in long, pliable needles, which sinter at 190°, m. p. 195—196° (corr.), $[\alpha]_D^{25}$ $-8{\cdot}8°$.

2 : 4 : 6-*Tribromophenol*-d-*glucoside* separates in slender, colourless needles, m. p. 207—208° (corr.), $[\alpha]_D^{26}$ $-23{\cdot}2°$. It is hydrolysed by emulsin.

[With JOSEF SEVERIN.]—*Allyl tetra-acetyl*-d-*glucoside* has m. p. 88—89°, $[\alpha]_D^{21}$ $-26{\cdot}3°$. On hydrolysis with barium hydroxide, *allyl*-d-*glucoside*, m. p. 102—103°, $[\alpha]_D^{20}$ $-42{\cdot}3°$, is obtained. The *dibromide* of the acetyl derivative has m. p. 87—88°, $[\alpha]_D^{21}$ $-11{\cdot}4°$. On treatment with bases, *monobromoallyl*-d-*glucoside* is obtained. E. F. A.

Arbutin and its Synthesis. CARL MANNICH (*Arch. Pharm.*, 1912, **250**, 547—560).—It is shown that commercial arbutin invariably contains some methylarbutin, and although pure methylarbutin can be obtained from this source, it is impossible to isolate pure arbutin. A synthesis of the latter is described.

Five commercial specimens of arbutin were found to contain from 5 to 40% of arbutin methyl ether as ascertained by methoxyl determinations. This is due to variation in the source of the material, bearberry leaves from Tyrol giving a product containing much arbutin methyl ether, whilst Spanish bearberry leaves yield a product containing not more than 5% arbutin methyl ether. Herissey's method for the separation of pure arbutin from the commercial article (Abstr., 1910, i, 692) does not yield a pure substance. Better results are obtained by precipitating the arbutin as its *additive product*,

$C_{18}H_{18}O_7N_4,2H_2O$, with hexamethylenetetramine, or by acetylating the crude product and recrystallising the mixed acetates from dilute alcohol, when penta-acetylarbutin, m. p. 143—144°, needles, separates first, but even by these methods a pure product is not obtainable. From commercial arbutin containing at least 40% of arbutin methyl ether, the latter can be separated in a pure state by precipitating most of the arbutin with hexamethylenetetramine, evaporating the mother liquor, and recrystallising the residue from dilute sodium hydroxide solution. Arbutin methyl ether separates with $1H_2O$ from water, or anhydrous from alcohol, melts at 158—160°, and re-melts at 175°. The *tetra-acetyl* derivative, m. p. 95·5—96·5°, crystallises from dilute alcohol in silky needles.

Acetylbromoglucose, prepared by van Charante's method (Abstr., 1902, i, 426), reacts with quinol in presence of alkali to give *tetra-acetylarbutin*, m. p. 136°, which crystallises from dilute alcohol in colourless prisms, and on acetylation yields penta-acetylarbutin, m. p. 144—145°, which on hydrolysis with baryta water yields arbutin. The latter crystallises from water with $1H_2O$ in colourless needles, with a bitter taste, melts at 163—164°, re-melts at 199·5—200° (corr.), and has $[\alpha]_D^{17\cdot5}$ $-60\cdot34°$ in water (compare Herissey, *loc. cit.*). T. A. H.

Phlorin, a Product of the Hydrolysis of Phloridzin. Max Cremer and R. W. Seuffert (*Ber.*, 1912, 45, 2565—2571).—When phloridzin is hydrolysed by dilute mineral acid, dextrose and phloretin are obtained, the latter substance being resolved by the action of potassium hydroxide solution into phloroglucinol and phloretic acid (*p*-hydroxy-α-phenylpropionic acid; Bougault, Abstr., 1900, i, 495). If, however, phloridzin is treated directly with an aqueous solution of an alkali (preferably barium hydroxide), the products of hydrolysis are phloretic acid and phlorin (phloroglucinol glucoside),

$$C_6H_3(OH)_2\cdot O\cdot C_6H_{11}O_5.$$

The last-mentioned substance, for which crystallographic details are given, is identical with the phloroglucinol glucoside synthesised by Fischer and Strauss (this vol., i, 884). D. F. T.

Fagopyrum-Rutin. Josef Brandl and G. Schärtel (*Arch. Pharm.*, 1912, 250, 414—417).—Fagopyrum-rutin is very easily and rapidly obtained as follows. Fresh, blooming buckwheat is repeatedly extracted with 98% alcohol for many days. The combined extracts are concentrated and freed from chlorophyll by Willstätter's process (Abstr., 1907, i, 71); the rutin is then isolated by concentrating the solution.

The leaves, flowers, and stalks of buckwheat yield respectively 1·78%, 0·71%, and 0·09% of fagopyrum-rutin. The hydrolysis of the rutin to quercitin and sugars (compare Wunderlich, Abstr., 1908, i, 559) is readily effected by boiling 40—50% sulphuric acid. C. S.

Saponin-like Glucosides from the Leaves of Polyscias nodosa and Hedera helix. A. W. van der Haar (*Arch. Pharm.*, 1912, 250, 424—435).—From the mixture of amorphous sapogenins,

dextrose, arabinose, and methylpentose obtained by the hydrolysis of the polyscias-saponins, the author has isolated a crystalline sapogenin, *polyscias-sapogenin*, $C_{26}H_{44}O_4$, m. p. 324°, α_D^{18} 75·58° in pyridine. It is a lactone, develops a characteristic violet-red coloration with concentrated sulphuric acid, yields two *substances*, m. p. 295° (not sharply) and 327° respectively, by sublimation, and closely resembles, but is not identical with, α-hederagenin described below.

The leaves of *Hedera helix* contain glucosides soluble in water and glucosides insoluble in water; the latter contain amorphous and crystalline components. From the last the author has isolated a crystalline glucoside, *α-hederin*, $C_{42}H_{66}O_{11}$, m. p. 256—257°, α_D^{10} 9·68° in alcohol. It crystallises with $2H_2O$, and, unlike other saponins, does not foam on shaking with water; however, it develops the characteristic saponin reaction (violet-red coloration) with concentrated sulphuric acid. It contains five hydroxyl groups and one methoxy-group, and is hydrolysed with difficulty by boiling 4% sulphuric acid, yielding equal molecular quantities of α-hederagenin, arabinose, and a methylpentose.

α-Hederagenin, $C_{31}H_{50}O_4$, m. p. 325—326°, forms rhombic crystals, and has α_D^{9} 81·2° in pyridine. It contains two hydroxyl groups and behaves like a lactone. By distillation with zinc dust in a current of hydrogen, it yields water and an oil, a portion of which is easily volatile with steam. This portion contains a *sesquiterpene*, $C_{15}H_{24}$, b. p. 245—255°, n^{13} 1·5303, which is optically inactive and develops a violet-red coloration with sulphuric acid. The portion of the oil which is not volatile with steam contains a *substance*, which is probably a hydrocarbon, $(C_5H_8)_x$. C. S.

Picrotoxin. II. JOHANNES SIELISCH (*Ber.*, 1912, **45**, 2555—2565. Compare this vol., i, 790).—Although acetone has been already observed as a degradation product of picrotoxin, it is obtainable more easily than hitherto suggested (compare Horrmann, this vol., i, 709). If picrotin, picrotoxinin, or picrotoxin is treated with *N*-potassium hydroxide solution at 100°, an equimolecular amount of acetone is formed. The hydrolysis of each of these substances can also be effected by concentrated hydrochloric acid, when the acetone is accompanied by a *substance*, $C_{12}H_{24}O_2$, m. p. 84°, b. p. 162°/12 mm., which by treatment with hydriodic acid and phosphorus in a sealed tube yields a *hydrocarbon*, $C_{12}H_{20}$, b. p. 90—100°.

Bromopicrotoxinin gives an *acetyl* derivative, needles, m. p. 268°. Although it is stable towards potassium permanganate, it is oxidised by nitric acid to a *substance* crystallising in needles, m. p. 184°; *acetyl* derivative, needles, m. p. 214°. The action of concentrated hydrochloric or hydrobromic acid on bromopicrotoxinin gives a monobasic *bromopicrotoxinic acid*, $C_{15}H_{19}O_8Br$ (termed β to distinguish it from the acid obtained by Meyer and Bruger, Abstr., 1899, i, 226), colourless needles, m. p. 223°. The α-bromopicrotoxinic acid (compare Meyer and Bruger) on heating with concentrated hydrochloric acid gives a *chlorobromopicrotoxinic acid*, $C_{14}H_{17}O_5ClBr{\cdot}CO_2H,H_2O$, leaflets, m. p. 274°; in a similar manner, α-bromopicrotoxininic acid, when heated with hydrobromic acid, adds a molecule of hydrogen bromide, yielding

dibromopicrotoxinic acid, $C_{14}H_{17}O_5Br_2 \cdot CO_2H,H_2O$, leaflets, m. p. 278° (decomp.). D. F. T.

Absorption of Ultra-violet Rays by α- and β-Chlorophylls and Crystallised Chlorophyll. Charles Dhéré and W. de Rogowski (*Compt. rend.*, 1912, 155, 653—656).—The α- and β-chlorophylls were obtained from the fresh leaves of *Taxus baccata* and the crystallised chlorophyll from those of *Galeopsis tetrahit.* The pure chlorophylls exhibit a remarkable transparency for the extreme ultra-violet rays. In ethereal solution, the natural chlorophylls only show one absorption band, which is exclusively ultra-violet, and is situated in the middle region of the ultra-violet spectrum considered ($\lambda = 304\mu\mu$ approximately). W. G.

Influence of Some Chemical Compounds on the Artificial Melanins. Maurice Piettre (*Compt. rend.*, 1912, 155, 594—597. Compare this vol., i, 42).—A study of some of the conditions governing the formation of artificial melanins. The yield of melanin varies with the weight of diastase or tyrosine used, but is not directly proportional to either. Mineral acids precipitate the melanins, 15 c.c. of *N*/10-hydrochloric acid per litre of solution being sufficient after forty-eight hours' contact with the diastase. Formic and acetic acid do not cause this precipitation. Alkalis produce no precipitation, but the hydroxides of the alkaline-earth metals bring about a rapid deposition of pigment. Hydrochloric acid precipitates the melanin without entering into combination, but with barium chloride there is a very considerable amount of barium in the precipitate, even after prolonged washing, and with the washing liquid, excess of barium hydroxide gives a yellow, flocculent precipitate containing a fairly constant percentage of barium. W. G.

Tannin and the Synthesis of Similar Substances. II. Emil Fischer and Karl Freudenberg (*Ber.*, 1912, 45, 2709—2726).—In continuation of their previous work (this vol., i, 471), the authors have investigated the action of pentamethyldigalloyl chloride on dextrose, and are led to the conclusion that the product obtained is a mixture, probably of two stereoisomeric penta-[pentamethyl-*m*-digalloyl] dextroses, the relative amounts of which depend on whether α- or β-dextrose is employed as starting point. It shows a very close analogy with methylotannin, which is also a mixture, but the identity of the two products could not be fully established. They consider their conjecture that pentadigalloyldextrose is an important constituent of tannin to have received additional confirmation.

3 : 5-Dimethylcarbonato-4-hydroxybenzoic acid was readily prepared from gallic acid (1 mol.), methyl chlorocarbonate (2 mols.), and sodium hydroxide. It had m. p. 186—187° (corr. decomp.) instead of 180°, as previously stated (Abstr., 1908, i, 892; 1911, i, 815). When, however, only 1 molecule of ethyl chlorocarbonate was employed for each molecule of gallic acid, a 36% yield of 3-*methylcarbonato*-4 : 5-*dihydroxybenzoic acid*, needles, m. p. 207° (corr. decomp.), was obtained. This acid, when treated with diazomethane and subsequently with sodium

hydroxide, yielded 5-hydroxy-3 : 4-dimethoxybenzoic acid, which, after purification by crystallisation of the *cadmium* salt, softened at 187° (corr.), and had m. p. 195—196° (corr.), whereas Herzig and Pollak found 189—192°. When heated in aqueous acetone solution with sodium hydroxide and 3 : 4 : 5-trimethoxybenzoyl chloride (m. p. 80°; Perkin and Weizmann, Trans., 1906, 89, 1655, give 78°), it gave 5(3′ : 4′ : 5′)-*trimethoxybenzoyloxy*-3 : 4-*dimethoxybenzoic acid*,

$$C_6H_2(MeO)_3\cdot CO\cdot O\cdot C_6H_2(OMe)_2\cdot CO_2H,$$

m. p. 194—195° (corr.). Phosphorus pentachloride transformed the latter in the presence of chloroform into the corresponding *chloride*, which softened at about 100° and had m. p. 110—111° (corr.), and from which the methyl ester, prisms, m. p. 129—130° (Mauthner, this vol., i, 267, gives 127—128°), was obtained by means of methyl alcohol. When the chloride was shaken with α-dextrose in the presence of chloroform and quinoline, a *product* was formed which, on analysis, gave figures intermediate between those required for penta-[pentamethyl-*m*-digalloyl]-dextrose and tetra-[pentamethyl-*m*-digalloyl]-dextrose. From analogy with the benzoyl and cinnamoyl derivatives of dextrose (see later), the authors regard the former constitution as the more probable. The product is amorphous, and does not give a sharp m. p. It begins to soften at about 125°, and forms clear drops at about 135°, which, on further heating, flow together. It is apparently not uniform. The analysed product had $[\alpha]_D^{25}$ +15·1° in benzene solution, whilst that recovered from the mother liquor showed $[\alpha]_D^{25}$ +28·1°. Attempts to isolate a substance of constant specific rotation were unsuccessful. Analogous results were obtained with the *product* of the action of pentamethyldigalloyl chloride on β-dextrose, the specific rotation of which was lowered by repeated crystallisation from $[\alpha]_D^{25}$ +19·5° to $[\alpha]_D^{21}$ +8·7° in acetylene tetrachloride solution. For purposes of comparison, a specimen of methylotannin was treated in the same manner as the above substances. Its behaviour was similar, $[\alpha]_D^{26}$ +14° observed for the original product sinking on repeated crystallisation to $[\alpha]_D^{21}$ +10·6° in acetylene tetrachloride solution.

The quinoline method has also been applied to the benzoylation of dextrose. Difficulty was experienced in obtaining substances of constant m. p α-*Pentabenzoyldextrose*, $[\alpha]_D^{25}$ +107·6° in chloroform, began to soften at about 145°, formed a viscid syrup at 157°, and showed a distinct meniscus at about 177°. β-Pentabenzoyldextrose had $[\alpha]_D^{24}$ +23·71° in chloroform, softened at about 155°, and was completely melted at 187° (corr.). It was probably identical with the pentabenzoyldextrose obtained by Fischer and Helferich (Abstr., 1911, i, 802).

α-*Pentacinnamoyldextrose*, on the other hand, crystallised without difficulty, and had $[\alpha]_D$ about +196° in chloroform, m. p. 225—226° (corr.). β-*Pentacinnamoyldextrose*, $[\alpha]_D$ −4·6° in chloroform, melted to a thick syrup at 191° (corr.), and showed a distinct meniscus at 201°.

Sucrose, when benzoylated under similar conditions, appeared to yield an *octabenzoyl* derivative. H. W.

The Tannin of Chinese Galls. KARL FEIST and HEINRICH HAUN (*Chem. Zeit.*, 1912, 36, 1201—1202).—It was thought that the

conflicting results obtained by various authors (Fischer and Freudenberg, this vol., i, 471; Manning and Nierenstein, this vol., i, 566) in the hydrolysis of tannin might be due to the use of gallo-tannin prepared from the two different sources of this product, namely, Turkish galls and Chinese galls. Feist has shown already that the former contain glucogallic acid and yield a tannin, which gives dextrose on hydrolysis (this vol., i, 566). It is now shown that Chinese galls contain gallic acid and a tannin, which yields dextrose on hydrolysis. A small proportion of this tannin is hydrolysed by dilute sulphuric acid only with difficulty. No glucogallic acid is present. T. A. H.

Active Principle of Iodotannin Solutions. C. COURTOT (*J. Pharm. Chim.*, 1912, [vii], 6, 253—258).—The author has shown previously (*ibid.*, 1911, [vii], 4, 299) that the iodotannin solution of the French Codex after treatment with hide powder does not invert sucrose, and must therefore contain its soluble iodine in the form of an organic compound (iodotannin), and not as hydriodic acid. In support of this conclusion it is now shown that residues left by slow evaporation of iodotannin solutions, previously cleared with hide powder, show under the microscope characteristic crystals of an unstable compound of gallic acid and iodine. T. A. H.

Isomerism of Some Unsaturated Lactonic Acids. ERICH BESCHKE, GEORG KÖHRES, and LUDWIG STOLL (*Annalen*, 1912, 391, 111—150).—Beschke, Winograd-Finkel, and Köhres (Abstr., 1911, i, 873) obtained by the interaction of zinc, benzil, and ethyl bromoacetate, the meso- and the racemic modifications of ethyl $\beta\gamma$-dihydroxy-$\beta\gamma$-diphenyladipate. By treatment with acid, the latter yields $\beta\gamma$-diphenylpentadilactone, whilst the meso-form is converted into ethyl β-hydroxy-$\beta\gamma$-diphenyl-γ-butyrolactone-γ-acetate, from which, through the intermediate formation of sodium $\beta\gamma$-diphenylmuconate, an unsaturated lactonic acid, $C_{18}H_{14}O_4$, was obtained. This acid was regarded as $\beta\gamma$-diphenyl-γ-crotonolactone-γ-acetic acid, because it yields undoubtedly the ester, m. p. 93°, of this acid by esterification with alcoholic hydrogen chloride. This view of the constitution of the acid is now shown to be erroneous, because the silver salt and ethyl iodide yield an *ethyl* ester, $C_{20}H_{18}O_4$, m. p. 73°.

The real *$\beta\gamma$-diphenyl-γ-crotonolactone-γ-acetic acid* [5-*keto*-2 : 3-*diphenyl*-2 : 5-*dihydrofuran-2-acetic acid*], $\begin{matrix}CO\text{——}O \\ CH{:}CPh\end{matrix}\!\!>\!CPh\cdot CH_2\cdot CO_2H$, m. p. 184° (which yields the ester, m. p. 93°, by both methods of esterification), has been obtained by warming the isomeric $\beta\gamma$-diphenylpentadilactone with glacial acetic acid and a little piperidine. It has also been prepared by hydrolysing by sodium hydroxide the racemic modification of ethyl $\beta\gamma$-dihydroxy-$\beta\gamma$ diphenyladipate and acidifying the resulting sodium γ-hydroxy-$\beta\gamma$-diphenyl-$\gamma\delta$-dihydromuconate.

Ethyl $\beta\gamma$-diphenyl-γ-crotonolactone-γ-acetate yields the corresponding acid by hydrolysis by glacial acetic and hydrochloric acids, and the isomeric lactonic acid (previously described as $\beta\gamma$-diphenyl-γ-crotonolactone-γ-acetic acid) by hydrolysis by alkali.

This isomeric lactonic acid has the same m. p. and similar crystalline form and solubilities as $\beta\gamma$-diphenyl-γ-crotonolactone-γ-acetic acid, and is easily converted into it by hydrogen bromide in glacial acetic acid. Taking into account its formation from sodium $\beta\gamma$-diphenylmuconate, the most probable constitution is that of *$\gamma\delta$-diphenyl-Δ^{β}-hexen-$\alpha\epsilon$-olid-ϵ-carboxylic acid*, $CH{<}{\begin{matrix}CPh{\cdot}CHPh\\CO\text{———}O\end{matrix}}{>}CH{\cdot}CO_2H$. This constitution explains quite satisfactorily the previously described behaviour of the acid (*loc. cit.*). The molecule easily suffers rearrangement at the lactone group, and therefore reacts as though it were $\beta\gamma$-diphenylmuconic acid, $CO_2H{\cdot}CH{:}CPh{\cdot}CPh{:}CH{\cdot}CO_2H$. Thus the reduction of the acid by zinc and acetic acid or by sodium amalgam in neutral or alkaline solution gives mainly $\beta\gamma$-diphenyldihydromuconic acid, m. p. 297°, together with a little of the isomeride, m. p. 185° (not 195°, as given previously), which probably has the *cis*-configuration. These isomeric acids do not combine additively with hydrogen bromide or bromine. The latter, however, attacks the sodium salts in aqueous solution to form *β-bromo-$\beta\gamma$-diphenyl-γ-butyrolactone-γ-acetic acid*,

$$\begin{matrix}CH_2{\cdot}CPhBr\\ |\\ CO\text{———}O\end{matrix}{>}CPh{\cdot}CH_2{\cdot}CO_2H,$$

m. p. 162°, and *$\beta\gamma$-dibromo-$\beta\gamma$-diphenylbutane*, $CPhMeBr{\cdot}CPhMeBr$, m. p. 152°.

Reduction of sodium diphenylmuconate by Paal's method gives the two isomeric $\beta\gamma$-diphenyladipic acids; the *cis*- and the *trans*-modifications of diphenyldihydromuconic acid have been treated in a similar manner, but only the former is attacked, yielding the diphenyladipic acid, m. p. 272°.

Diphenylcrotonolactone-acetic acid is scarcely attacked by zinc and acetic acid. It is reduced, however, by sodium amalgam, yielding *γ-hydroxy-$\beta\gamma$-diphenyladipic acid*,

$$CO_2H{\cdot}CH_2{\cdot}CHPh{\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2H,$$

m. p. 195—198°, in alkaline solution, and *$\beta\gamma$-diphenylbutyrolactone-γ-acetic acid* [*5-keto*-2 : 3-*diphenyltetrahydrofuran-2-acetic*],

$$\begin{matrix}CH_2{\cdot}CHPh\\ |\\ CO\text{———}O\end{matrix}{>}CPh{\cdot}CH_2{\cdot}CO_2H,$$

m. p. 221° (*ethyl* ester, m. p. 116°), in neutral solution. The latter acid is converted into 2 : 8-diacetoxychrysene by acetic anhydride and concentrated sulphuric acid. The reduction of sodium diphenylcrotonolactone-γ-acetate by hydrogen and colloidal palladium yields $\beta\gamma$-diphenylbutyrolactone-γ-acetic acid, whilst diphenylhexenolidecarboxylic acid gives the two isomeric diphenyladipic acids by similar treatment.

Diphenylcrotonolactone-γ-acetic acid and the hexenolide acid are only difficultly attacked by potassium permanganate, and do not reduce ammoniacal silver oxide. In glacial acetic acid containing sodium acetate, both are attacked by bromine on the water-bath, and yield *α-bromo-$\beta\gamma$-diphenylcrotonolactone-γ-acetic acid*,

$$\begin{matrix}CBr{:}CPh\\ |\\ CO\text{——}O\end{matrix}{>}CPh{\cdot}CH_2{\cdot}CO_2H,$$

m. p. 168° (*ethyl* ester, m. p. 119—120°). The hexenolide acid and bromine in boiling chloroform yield *β-bromo-$\gamma\delta$-diphenyl-Δ^{β}-hexen-*

αε-olid-ε-carboxylic acid, $CBr<\begin{matrix}CPh\cdot CHPh\\CO\text{———}O\end{matrix}>CH\cdot CO_2H$, m. p. 186°. These two brominated compounds are more easily obtained by the action of aqueous bromine at 0° on the sodium salt of diphenylcrotonolactone-γ-acetic acid and of diphenylmuconic acid respectively. The *ethyl* ester, m. p. 143°, of the bromohexenolide acid is obtained from the silver salt of the acid and ethyl iodide, or by the action of bromine on a chloroform solution of ethyl hydrogen diphenylmuconate in sunlight.

An alcoholic suspension of the ethyl ester of either of these brominated acids, when gently warmed with sodium ethoxide and then acidified, yields *ethyl hydrogen α-bromo-βγ-diphenylmuconate*,

$$CO_2H\cdot CBr:CPh\cdot CPh:CH\cdot CO_2H,$$

m. p. 152—153°. The *diethyl* ester, $C_{20}H_{17}O_4Br$, m. p. 122—123°, is obtained therefrom by alcoholic hydrogen chloride. C. S.

Two New Methods of Formation of Dyes of the Pyronine Group. JOACHIM BIEHRINGER [and R. GLÜCKSBERG and A. TANZEN] (*Annalen*, 1912, **391**, 308—325).—An intimate mixture of benzil (1 mol.) and dimethyl-*m*-aminophenol (2 mols.) is heated for four to five hours on the water-bath in an atmosphere of carbon dioxide. The products are benzoic acid, benzoin, and a substance which is shown to be identical with Heumann and Rey's tetramethylrosamine (the tetramethylbenzorhodamine of the Badische Co.), and with the tetramethylbenzopyronine obtained from benzaldehyde and dimethyl-*m*-aminophenol.

Dimethyl-*m*-aminophenol is heated with concentrated sulphuric acid at 160—170° for five to six hours. The aqueous solution of the product is neutralised by sodium carbonate, whereby a bluish-red colour base is obtained, which dissolves in dilute mineral acids with a bluish-red colour and orange-yellow fluorescence. By solution in dilute hydrochloric acid and treatment with a little ferric chloride, the colour base is converted into a dye, which is shown to be s-*dimethylformopyronine*, $NHMe\cdot C_6H_3<\begin{matrix}CH\\O\end{matrix}>C_6H_3:NHMeCl$, by its formation from alcoholic methyl-*m*-aminophenol and 30% formaldehyde. The zincichlorides of the dye prepared by the two methods show identical absorption spectra, whilst the *leuco-base*, $C_{15}H_{16}ON_2$, m. p. 192—193°, colourless needles, obtained by distilling a mixture of the dye, sand, zinc dust, and soda-lime, or by treating the dye with dilute hydrochloric acid and zinc dust, forms a *platinichloride*,

$$C_{15}H_{16}ON_2,H_2PtCl_6,$$

yellow needles. C. S.

Oxonium Compounds. I. Tricyclic Benzopyrylium Compounds. WALTHER BORSCHE and A. GEYER (*Annalen*, 1912, **393**, 29—60).—Tricyclic benzopyrylium compounds in the form of their chlorides can be obtained in one operation by condensing *o*-hydroxylated benzaldehydes and cyclic ketones (which are capable of condensing

with aldehydes) by hydrogen chloride, or in two operations by obtaining first an unsaturated hydroxy-ketone from the two components in alkaline solution, and then dehydrating it by hydrogen chloride.

Thus equal molecular quantities of salicylaldehyde and methyl*cyclo*hexan-3-one in alcohol are kept with aqueous sodium hydroxide for about a week, whereby 4-*salicylidene*-1-*methyl*cyclo*hexan-3-one*, $OH\cdot C_6H_4\cdot CH:C<\substack{CH_2\cdot CH_2 \\ CO-CH_2}>CHMe$, m. p. 153°, yellow needles, is obtained, the *sodium* salt of which is red. 6-*Salicylidene*-1 : 3-*dimethyl*-Δ^3-cyclo*hexen*-5-*one*, $C_{15}H_{16}O_2$, m. p. 179°, dark yellow plates, is obtained in a similar manner from 1 : 3-dimethyl-Δ^3-*cyclo*hexen-5-one. Under similar conditions, pulegone yields, not a similarly constituted compound, but the di-sodium derivative of dihydroxystyryl ketone, which owes its formation probably to a decomposition of the pulegone into acetone and methyl*cyclo*hexan-3-one.

By keeping an alcoholic solution of *cyclo*hexanone and salicylaldehyde with 20% sodium hydroxide for two days and then treating with carbon dioxide, 2 : 6-*disalicylidene*cyclo*hexanone*, $C_{20}H_{18}O_3$, m. p. 150°, yellow needles, is obtained. By heating alone or with dissociating solvents, it is rapidly changed to the trimethylenedibenzo*spiro*pyran, m. p. 159° (see below). In a similar manner, methyl*cyclo*hexan-4-one yields 3 : 5-*disalicylidene*-1-*methyl*cyclo*hexan*-4-*one*, $C_{21}H_{20}O_3$, m. p. 159—160° (decomp.), pale yellow crystals, which is converted by boiling aqueous alcohol through the isomeric benzopyranol into the methyltrimethylenedibenzo*spiro*pyran (see below). By keeping with 20% sodium hydroxide for two weeks, an alcoholic solution of suberone and salicylaldehyde (2 mols.) yields the dark red *disodium* derivative of 2 : 7-*disalicylidene*cyclo*heptanone*, $C_{21}H_{20}O_3$, m. p. 155°, yellow leaflets, which cannot be converted into the corresponding dibenzo*spiro*pyran by boiling with dilute alcohol.

3-*Methyl*-1 : 2 : 3 : 4-*tetrahydro-xanthylium chloride*,

$$C_6H_4<\substack{CH \\ OCl}\geqslant C_6H_7Me,$$

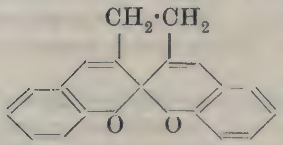
which is produced almost instantly by saturating a solution of 4-salicylidene-1-methyl*cyclo*hexan-3-one in cold glacial acetic acid with hydrogen chloride, can only be isolated from the acetic acid solution in the form of the *ferrichloride*, $C_{14}H_{15}OCl,FeCl_3$, m. p. 114—115° (decomp.), brownish-yellow needles, or the *tri-iodide*, $C_{14}H_{15}OI_3$, m. p. 135°, dark reddish-brown needles. By treating its acetic acid solution with aqueous sodium acetate, the chloride is converted into the *benzopyranol*, $C_6H_4<\substack{CH:C\cdot CH_2\cdot CH_2 \\ O-C(OH)\cdot CH_2}>CHMe$, m. p. about 90°, green powder containing H_2O, which is stable to boiling 25% alcoholic sodium hydroxide, is re-converted into the xanthylium chloride by hydrogen chloride in glacial acetic acid, and yields 3-methylxanthene by distillation with zinc chloride.

2 : 3-α-*Salicylidenetrimethylenebenzopyrylium chloride*,

$$C_6H_4<\substack{CH:C\cdot CH_2 \text{———} CH_2 \\ OCl:C\cdot C(:CH\cdot C_6H_4\cdot OH)}>,$$

m. p. 181—183° (decomp.), red crystals containing $1\frac{1}{2}H_2O$, is obtained

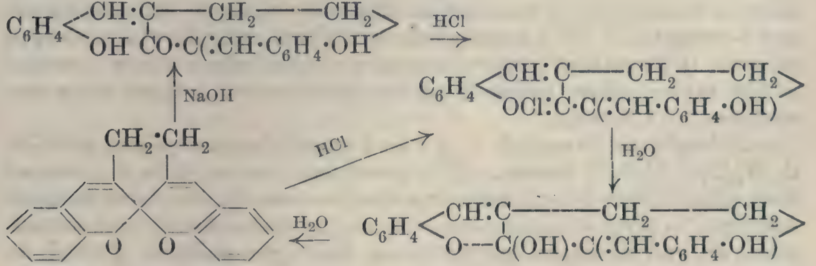
by treating a glacial acetic acid solution of 2 : 5-disalicylidene*cyclo*pentanone with hydrogen chloride, or, much more conveniently, by similarly treating a cold solution of *cyclo*pentanone and salicylaldehyde (2 mols.). By treating salicylidenetrimethylenebenzopyrylium chloride in almost boiling alcohol with aqueous sodium acetate, it is converted into 3 : 3′-*ethylenedibenzo*spiro*pyran* (annexed formula), m. p. 218—219°, glistening crystals [the *carbinol*,



$$C_6H_4<\begin{matrix}CH:C\cdot CH_2\cdot CH_2\\ O-C(OH)\cdot C:CH\cdot C_6H_4\cdot OH\end{matrix}$$

is obtained as a by-product], which is converted into salicylidenetrimethylenebenzopyrylium chloride by hydrogen chloride in glacial acetic acid, and into 2 : 5-disalicylidene*cyclo*pentanone by warm alcoholic sodium hydroxide.

The changes which the preceding substances undergo, and are similar to those exhibited by the following compounds, are clearly illustrated by the scheme :



Methyl*cyclo*pentan-3-one and salicylaldehyde (2 mols.) in glacial acetic acid react in the presence of hydrogen chloride to form 2 : 3-*α-salicylidene-β*(or *γ*)*-methyltrimethylenebenzopyrylium chloride*,

$$C_6H_4<\begin{matrix}CH:C\cdot CHMe—CH_2\\ OCl:C\cdot C(:CH\cdot C_6H_4\cdot OH)\end{matrix}> \text{ or }$$

$$C_6H_4<\begin{matrix}CH:C\cdot CH_2—CHMe—\\ OCl:C\cdot C(:CH\cdot C_6H_4\cdot OH)\end{matrix}>,$$

decomp. 142°, yellow crystals, which is converted by boiling aqueous alcoholic sodium acetate into the *carbinol*, and ultimately into 3 : 3′-*propylenedibenzo*spiro*pyran*, $C_{20}H_{16}O_2$ (constitution similar to that above), decomp. 254—255°, colourless crystals.

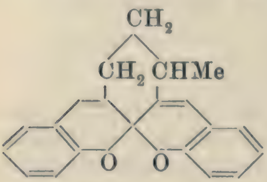
4-*Salicylidene*-1 : 2 : 3 : 4-*tetrahydro-xanthylium chloride*,

$$C_6H_4<\begin{matrix}CH\\ OCl\end{matrix}>C_6H_6:CH\cdot C_6H_4\cdot OH,$$

m. p. 155° (decomp.), dark brown plates containing $1\frac{1}{2}H_2O$, is obtained by treating 2 : 6-disalicylidene*cyclo*hexanone in glacial acetic acid with hydrogen chloride or directly in a similar manner from *cyclo*hexanone and salicylaldehyde, or by fission of the corresponding dibenzo*spiro*pyran by hydrogen chloride in warm glacial acetic acid. It forms a *ferrichloride*, $C_{20}H_{17}O_2Cl,FeCl_3$, decomp. about

142°, dark red needles with green reflex, and is converted, by boiling its acetic acid solution with 90% alcohol, into 3 : 3′-*trimethylenedibenzo*spiro*pyran*, $C_{20}H_{16}O_2$, m. p. 159°, stout needles, which is re-converted into the xanthylium chloride and the disalicylidene*cyclo*hexanone by the methods given above.

4-*Salicylidene-3-methyl*-1 : 2 : 3 : 4-*tetrahydro-xanthylium chloride*, $C_{21}H_{19}O_2Cl,1\frac{1}{2}H_2O$, m. p. 119—120°, dark red, crystalline powder, obtained by condensing salicylaldehyde and *d*-methyl*cyclo*hexan-3-one in ether by hydrogen chloride, forms a *ferrichloride*, $C_{21}H_{19}O_2Cl,FeCl_3$, m. p. 152°, black needles with green reflex and red streak, and is converted by water into as-*methyl*-3 : 3′-*trimethylenedibenzo*spiro*pyran* (annexed formula), m. p. 147°, colourless needles, which is re-converted into the xanthylium chloride by hydrogen chloride in ether or glacial acetic acid, but apparently does not yield 2 : 4-disalicylidene-1-methyl*cyclo*hexan-3-one even by prolonged boiling with alcoholic sodium hydroxide.



Since 4-salicylidene-3-methyl-1 : 2 : 3 : 4-tetrahydro-xanthylium chloride is obtained by treating an ethereal solution of salicylaldehyde and 3-methyl-1 : 2 : 3 : 4-tetrahydro-xanthylium chloride with hydrogen chloride, it seems that in pyrylium salts the methylene group attached to the carbon atom adjacent to the quadrivalent oxygen atom can condense with ketones.

4-*Salicylidene-2-methyl*-1 : 2 : 3 : 4-*tetrahydro-xanthylium chloride*, $C_{21}H_{19}O_2Cl,1\frac{1}{2}H_2O$, decomp. 155°, greenish-yellow crystals, is obtained from salicylaldehyde and methyl*cyclo*hexan-4-one in the usual manner. Attempts to prepare a salicylidenebenzopyrylium chloride from salicylaldehyde and suberone by means of hydrogen chloride yielded an almost colourless *substance*, $C_{21}H_{18}O_2$, which is apparently 3 : 3′-*tetramethylenedibenzo*spiro*pyran*; however, it is not affected by hydrogen chloride in glacial acetic acid or by warm alcoholic sodium hydroxide.

C. S.

Thiophen and Furan Derivatives. OSCAR HINSBERG (*Ber.*, 1912, **45**, 2413—2418. Compare Abstr., 1910, i, 334).—The prolonged action of ethyl thiodiglycollate, glyoxal, and alcoholic sodium ethoxide results in the formation, after acidification, of thiophen-2 : 5-dicarboxylic acid. In a similar manner, ethyl thiodiglycollate, alcoholic sodium ethoxide, and ethyl oxomalonate yield, after successive acidification and hydrolysis of the product by boiling 10% sodium hydroxide, 2-*ethyl dihydrogen* 3-*hydroxythiophen*-2 : 4 : 5-*tricarboxylate*,

$$S<\begin{matrix}C(CO_2Et):C\cdot OH \\ \qquad\qquad\quad | \\ C(CO_2H):C\cdot CO_2H\end{matrix},$$

m. p. 188°, colourless needles, which develops a cherry-red coloration with ferric chloride and forms a *sodium* salt, $C_9H_7O_7SNa,H_2O$, long needles, decomp. about 260°.

By boiling methyl 3 : 4-dihydroxythiophen-2 : 5-dicarboxylate with dilute alcoholic sodium hydroxide (4 mols.) and acidifying the product,

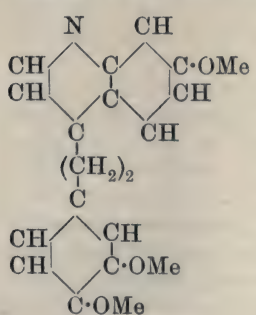
methyl 3 : 4-*dihydroxythiophen*-2-*carboxylate*, $S<\begin{matrix}C(CO_2Me):C\cdot OH \\ CH=\!=\!=C\cdot OH\end{matrix}$, m. p. 108° (?), is obtained, which develops a blue coloration with ferric chloride; the corresponding *ethyl* ester has m. p. 76—78°.

Methyl thiodiglycollate, ethyl oxalate, and methyl alcoholic sodium methoxide yield ultimately *methyl* 3 : 4-*dihydroxyfuran*-2 : 5-*dicarboxylate*, m. p. 220°. Methyl thiodiglycollate, benzil, and sodium methoxide in a similar manner yield 3 : 4-*diphenylfuran*-2-*carboxylic acid*, m. p. 231°. By a similar process with phenanthraquinone, *phenanthrafurandicarboxylic acid dihydrate*, $C_{18}H_{14}O_7$, decomp. 280°, is obtained, from which the two molecules of water are not expelled at 130°. C. S.

Solubility of Alkaloids in Basic Solvents. MAX SCHOLTZ (*Arch. Pharm.*, 1912, **250**, 418—423).—The solubility of alkaloids in basic solvents, such as aniline, pyridine, piperidine, and diethylamine, has been determined; a table of the results is given. It has been found that alkaloids differ in a remarkable degree as regards their solubility in one and the same basic solvent. As an illustration, the following solubilities in pyridine are given, the numbers in brackets representing the parts by weight of the alkaloid dissolved by 100 parts by weight of pyridine at 20°: quinine (101), cinchonine (1·4), strychnine (1·5), brucine (28), morphine (19), narcotine (2·3), papaverine (8), thebaine (9), veratrine (175), cocaine (80), atropine (73). Some of the solubilities are extremely striking; thus the solubility of veratrine in diethylamine is 271, whilst strychnine, which is generally so sparingly soluble in most solvents, dissolves in only five times its weight of aniline at 20°. The solubilities of alkaloids in basic solvents at their b. p. are very much greater than at the ordinary temperature.

Although sodium and potassium hydroxides, as is well known, diminish the solubility of organic bases in water, the author finds that quinine, strychnine, and cinchonine are decidedly more soluble in 10% ammonia than in water. This is true, however, only with aqueous ammonia; the alkaloids are less soluble in alcoholic ammonia than in alcohol. C. S.

Angostura Alkaloids. JULIUS TRÖGER and W. KROSEBERG (*Arch. Pharm.*, 1912, **250**, 494—531. Compare Abstr., 1911, i, 482).—It was found that mixtures of cusparine and galipine could be separated by conversion into the oxalates, cusparine oxalate being insoluble and galipine oxalate soluble in water. Making use of this method only three alkaloids, cusparine, galipine, and galipoidine, could be prepared from angostura bark extract, so that the supposed alkaloids, cusparidine and galipidine, are probably only mixtures of galipine and cusparine. On oxidation with permanganate, galipine yields veratric acid and a methoxyquinolinecarboxylic acid, and the annexed formula is provisionally assigned to this alkaloid.



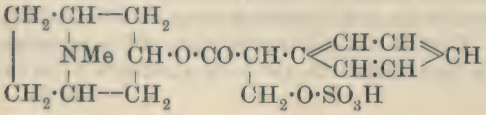
Nitrogalipine, $C_{20}H_{20}O_3N,NO_2$, m. p. 140°, formed by the action of either dilute or concentrated nitric acid on galipine, crystallises in pale yellow needles, yields a *nitrate*, m. p. 180° (decomp.), crystallising in bright yellow, prismatic needles, a *hydrochloride*, $B,HCl,\frac{1}{2}H_2O$, m. p. 180° (decomp.), a *sulphate*, B_2,H_2SO_4,H_2O, m. p. 191° (decomp.), a *platinichloride*, m. p. 227° (decomp.), and an *aurichloride*, m. p. 192° (decomp.). On reduction with stannous chloride and hydrochloric acid in alcohol, *aminogalipine* is produced; this crystallises in grey needles, m. p. 156°, and yields a *platinichloride*, which darkens at 192°, and does not melt below 300°.

On oxidation with permanganate in alkaline solution, galipine sulphate yields veratric acid and an *acid*, $C_{11}H_9O_3N,2H_2O$, m. p. 194° (anhydrous), crystallising in glancing needles, which contains one methoxyl group and is probably a methoxyquinolinecarboxylic acid, since on heating at 190° it gives a product from which a *platinichloride*, m. p. 221°, having the composition of a methoxyquinoline platinichloride, was prepared. With hydriodic acid, it gives an *acid* (? hydroxyquinolinecarboxylic acid), $C_{10}H_7O_3N$, m. p. 273° (decomp.), crystallising in long, slender, colourless needles.

Galipine on destructive distillation with zinc dust yields quinoline, which was identified by means of the platinichloride.

Galipine is colourless when pure, and yields colourless salts; the yellow colour usually ascribed to the salts is due to the presence of impurities. T. A. H.

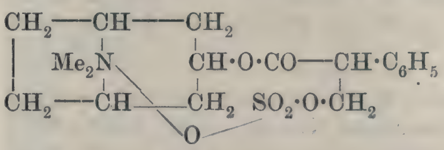
Preparation of Sulphuric Acid Esters of Alkylamine Hydroxy-acid Esters. F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 247455 and 247457).—The action of concentrated sulphuric acid on alkylamine hydroxy-acid esters has been described (Abstr., 1893, i, 677; 1894, i, 153), and in this connexion the following compounds have been obtained.



Atropinesulphuric acid (annexed formula), prisms, m. p. 238—239°, is prepared by dissolving atropine sulphate (m. p. 183—184°) in 97% sulphuric acid, and allowing it to remain during one hour at the ordinary temperature; the solution is diluted, and carefully treated with ammonium hydroxide, when the ester is precipitated in crystalline form.

The *compound*, slender needles, obtained when a solution of scopolamine in carbon tetrachloride is cooled and allowed to remain in contact with fuming sulphuric acid during half an hour, has m. p. 225°, whilst homoatropine hydrobromide, under similar conditions, furnishes *homoatropinesulphuric acid*, rhombic leaflets or prisms, containing H_2O, and m. p. 245° (when anhydrous). These esters crystallise from hot water. The second patent states that the sulphuric acid employed in the preceding reactions can be replaced by chlorosulphonic acid. F. M. G. M.

Preparation of Sulphuric Acid Esters of Alkylammonium Salts of Hydroxy-acid Esters of Alkylamines. F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 247456. Compare Abstr., 1903, i, 512, and preceding abstract).—The previously described atropine esters have been found to undergo internal salt formation.



Methylatropiniumsulphuric acid (annexed formula) forms glistening leaflets, m. p. 223—225°.

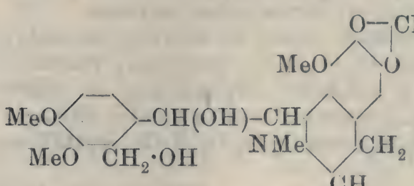
Methylscopolaminium iodide, colourless prisms, m. p. 216—217°, is prepared by the action of methyl iodide on scopolamine in absolute alcoholic solution; on treatment with silver sulphate it yields *methylscopolaminium sulphate*, an amorphous mass, which furnishes *methylscopolaminiumsulphuric acid* (prismatic crystals, m. p. 238—241°) with fuming sulphuric acid.

F. M. G. M.

Nicotine and Water. HUGO R. KRUYT (*Chem. Weekblad*, 1912, 9, 830—834).—The author could not find any trace of the change in the specific rotation of mixtures of water and nicotine, such as was described by Pribram (Abstr., 1887, 755). Distillation in an atmosphere of hydrogen under reduced pressure yields pure nicotine, but the alkaloid could not be obtained crystalline. A. J. W.

The Electrolytic Reduction of Narcotine. CESARE FINZI and MARTIN FREUND (*Ber.*, 1912, 45, 2322—2333).—By the reduction of narcotine at a lead cathode, there has been obtained among other substances, hydrodeoxynarcotine, $C_{22}H_{25}O_6N$, m. p. 126° (Hammel, *Diss.*, 1910).

Attempts by the present authors to reproduce the same results have hitherto failed. The reduction of narcotine in dilute sulphuric acid at a lead cathode gave a mixture of a syrupy product with a crystalline substance, prisms, m. p. 128°, quite distinct from the above substance; its behaviour indicates it to be *tetrahydronarcotine*, $C_{22}H_{27}O_7N$; *hydrochloride*, decomposes at 160—165°; *platinichloride*, yellow, amorphous powder. The *methiodide*, needles, m. p. 224° (decomp.), on treatment with silver oxide gives an oily *base* (*A*), which on further treatment with potassium hydroxide gives ψ-meconinic acid (compare Perkin, Trans., 1890, 77, 1073), together with a yellow oily *base*, $C_{13}H_{19}O_3N$,(*B*),*hydriodide*, prismatic needles, m. p. 194°; the *methiodide*, m. p. 192—193°, yields trimethylamine when warmed with a solution of sodium ethoxide.



(I.)

Oxidation of the above tetrahydronarcotine with potassium dichromate and dilute sulphuric acid gives ψ-meconinic acid and cotarnine.

On heating with benzoic anhydride, tetrahydronarcotine is converted into an oily *dibenzoyl* derivative, the crystalline *platinichloride* of

which on hydrolysis with alcoholic potassium hydroxide yields two molecules of benzoic acid.

From the above results the conclusion is drawn that the base *B* is 6-*methoxy*-4:5-*methylenedioxy*-1-*methyl*-2-*dimethylaminoethylbenzene*, $OMe\cdot C_6HMe(CH_2O_2)\cdot CH_2\cdot CH_2\cdot NMe_2$, whilst to tetrahydronarcotine is attributed the structure given in formula (I); the base *A* is the quaternary dimethylammonium hydroxide derived from this structure.

D. F. T.

Methylation of Clupeine. F. Rogoziński (*Zeitsch. physiol. Chem.*, 1912, 80, 371—375).—Skraup and Krause (Abstr., 1909, i, 748), have shown that a profound change takes place in the protein molecule when methyl iodide acts on casein. Methyl sulphate is shown to have a similar effect on clupeine, the arginine nitrogen, which before treatment corresponded with 88% of the total, sinking after methylation to 37·7% and 28·8% in the methylated product. E. F. A.

Strychnos Alkaloids. XV. Decomposition of Brucine into a Base, termed Curbine. Hermann Leuchs and George Peirce (*Ber.*, 1912, 45, 2653—2662).—The acid, $C_{23}H_{24}O_9N_2$ (acetylbrucinolic acid), isolated from the oxidation product of brucinolone acetate (Leuchs and Brewster, this vol., i, 210), is hydrolysed by hydrochloric acid to acetic acid, malonic acid, and a base, *curbine*, $C_{18}H_{20}O_5N_2$, which crystallises in slender needles, m. p. 322°, gives a red coloration with nitric acid, and has also been obtained by hydrolysing the substance, $C_{22}H_{24}O_7N_2$, formed by the removal of carbon dioxide from acetylbrucinolic acid; the *hydrochloride* crystallises in colourless needles, m. p. 270°, with previous darkening at 265°. In addition to the above compounds, a small amount of a *hydrochloride*, crystallising in yellow leaflets, m. p. 238—240° (decomp.), was isolated from the product of hydrolysis of acetylbrucinolic acid. From these results the authors draw the conclusion that brucinolone acetate contains the groups shown in (I) below, and represent its conversion into acetylbrucinolic acid and curbine by the following scheme:

$$\text{I.}\quad \begin{array}{l} :N\cdot CO{-}CH_2 \\ \vdots C\!\!>\!C{=}CH \\ \vdots C \\ :CH\cdot OAc \end{array} \longrightarrow \begin{array}{l} :N\cdot CO\cdot CH_2\cdot CO_2H \\ \vdots C\!\!>\!CO \\ \vdots C \\ :CH\cdot OAc \end{array} \longrightarrow \begin{array}{l} :NH \\ \vdots C\!\!>\!CO \\ \vdots C \\ :CH\cdot OH. \end{array}$$

The compound $C_{22}H_{24}O_7N$ is the diacetyl derivative of curbine.

The oxidation of brucinolone acetate yields, in addition to acetylbrucinolic acid and the compound, $C_{23}H_{22}O_6N_2$, previously described (*loc. cit.*), a small amount of a *substance*, crystallising in yellow prisms, m. p. 230—235° (decomp.), together with a yellow, oily *acid*, the *barium* salt of which, $C_{23}H_{22}O_{10}N_2Ba$ or $C_{23}H_{24}O_{10}N_2Ba$, crystallises in slender, white needles.

The by-product, $C_{21}H_{24}O_6N_2$, obtained by the action of sodium hydroxide on brucinolic acid, is converted by the further action of sodium hydroxide into brucinolone, which is accompanied by small amounts of the following substances: (1) A *compound*, $C_{21}H_{22}O_5N_2$, isomeric with brucinolone, and termed by the authors *crypto*-

brucinolone; it crystallises in lustrous, yellow, broad prisms, m. p. 188—190°, and yields a *hydrochloride*, crystallising in needles, m. p. 240°. (2) A *substance*, $C_{21}H_{24}O_6N_2,6H_2O$, which forms lustrous, broad needles or leaflets, m. p. 227—228°, with previous sintering at 220°.

F. B.

Pyrroline-2-carboxylic Acid. EMIL FISCHER and FERDINAND GERLACH (*Ber.*, 1912, **45**, 2453—2456. Compare Fischer and van Slyke, Abstr., 1911, i, 1020).—By reduction of pyrrole-2-carboxylamide with phosphonium iodide and concentrated hydrogen iodide, a compound containing two hydrogen atoms more, namely, *pyrroline-2-carboxylic acid*, is obtained. This is very similar to proline, and the two acids may readily be mistaken for one another. It is proposed to make a special search for pyrroline-2-carboxylic acid among the products of protein hydrolysis. The free acid has m. p. 235° (corr.); the *copper* salt, $C_{10}H_{12}O_4N_2Cu,2H_2O$, consists of microscopic, irregular, intergrown, deep blue plates. The *methyl* ester resembles those of the aliphatic amino-acids.

E. F. A.

2:3-Dimethylpyrrole. OSCAR PILOTY and K. WILKE (*Ber.*, 1912, **45**, 2586—2592).—Ethyl oxalacetate condenses with β-aminobutan-γ-one in alkaline solution, yielding 4-*ethyl hydrogen* 2 : 3-*dimethylpyrrole*-4 : 5-*dicarboxylate*, $NH<\begin{matrix}CMe{=\!=}CMe\\ C(CO_2H){:}C{\cdot}CO_2Et\end{matrix}$, which crystallises in small, stout prisms, m. p. 201°, and forms with potassium methoxide in methyl alcoholic solution a *potassium* salt, crystallising in snow-white needles of a pearly lustre. The acid ester is converted by methyl sulphate into the *methyl ethyl* ester, stout, colourless prisms, m. p. 152°, and is hydrolysed by aqueous potassium hydroxide to 2 : 3-*dimethylpyrrole*-4 : 5-*dicarboxylic acid*, which becomes red at 180°, sinters at 200°, and melts at 225° with evolution of carbon dioxide. When boiled with aqueous potassium hydroxide for twenty hours, it yields 2 : 3-*dimethylpyrrole*-4-*carboxylic acid*, $NH<\begin{matrix}CMe{:}CMe\\ CH{=}C{\cdot}CO_2H\end{matrix}$, m. p. 188°, the *ethyl* ester of which has m. p. 110—111°, and is best prepared by heating the original monoethyl ester at 225° in an atmosphere of carbon dioxide.

Ethyl tetramethylpyrocolldicarboxylate,

$$CMe<\begin{matrix}C(CO_2Et){:}C{\cdot}CO{\cdot}N{-\!-\!-}CMe\\ CMe{-\!-\!-}N{\cdot}CO{\cdot}C{:}C(CO_2Et)\end{matrix}>CMe,$$

is obtained in long, pointed, light yellow, felted needles of a silky lustre, m. p. 169°, by boiling 4-ethyl hydrogen 2 : 3-dimethylpyrrole-4 : 5-dicarboxylate with acetic anhydride.

When heated with potassium and toluene, ethyl 2 : 3-dimethylpyrrole-4-carboxylate forms a *potassium* derivative, which reacts with acetyl chloride, yielding *ethyl* 1-*acetyl*-2 : 3-*dimethylpyrrole*-4-*carboxylate*, spherical aggregates of pale red needles, m. p. 65°.

2 : 3-Dimethylpyrrole, obtained together with a small amount of bis-2 : 3-dimethylpyrrole (compare this vol., i, 736; Dennstedt, Abstr., 1899, 1209) by the distillation of 2 : 3-dimethylpyrrole in

a current of carbon dioxide at a temperature slightly above its m. p., forms a *potassium* derivative, which reacts with ethyl iodide, yielding an *ethyl* derivative, in which the ethyl group is probably attached to one of the carbon atoms of the ring.

4-*Ethyl hydrogen 2-methyl-3-ethylpyrrole*-4 : 5-*dicarboxylate*,

$$NH<\begin{matrix} CMe{=\!=}CEt \\ C(CO_2H){:}C{\cdot}CO_2Et \end{matrix}$$

prepared by condensing ethyl oxaloacetate with β-aminopentan-γ-one in alkaline solution, has m. p. 174—175°. F. B.

An Attempt to Synthesise 2 : 3-Dimethyl-4-ethylpyrrole (Hæmopyrrole). LUDWIG KNORR and KURT HESS (*Ber.*, 1912, **45**, 2626—2631).—By the reduction of β-oximinobutan-γ-one and the sodium salt of formylacetone with sodium amalgam in alcoholic solution, the authors have obtained 4-formyl-2 : 3 : 5-trimethylpyrrole instead of the expected 2 : 3-dimethyl-4-ethylpyrrole.

In the first attempts the usual method of reduction adopted in Knorr's synthesis of pyrrole derivatives was employed, namely, reduction with zinc dust and glacial acetic acid, but owing to the ease with which formylacetone condenses in the presence of acids to triacetylbenzene, no pyrrole compound was obtained. It was found subsequently that the pyrrole synthesis may be accomplished by reduction with sodium amalgam in alcoholic solution, and in illustration of the latter method of reduction the preparation of ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate and 2-carbethoxy-3 : 5-dimethylpyrrole-4-carboxylanilide is described.

4-*Formyl*-2 : 3 : 5-*trimethylpyrrole*, $\begin{matrix} CMe{-\!-}C{\cdot}CHO \\ \| \qquad\quad \| \\ CMe{\cdot}NH{\cdot}CMe \end{matrix}$, has m. p. 80°, b. p. 186·5°, reduces ammoniacal silver nitrate, and forms a *phenylhydrazone*, crystallising in yellow needles. F. B.

Acetylpyrroles. LUDWIG KNORR and KURT HESS (*Ber.*, 1912, **45**, 2631—2635).—It has been shown previously (Abstr., 1911, i, 1019) that the hydrazone of 3-acetyl-2 : 4-dimethylpyrrole when heated with sodium ethoxide yields 3-acetyl-2 : 4-dimethylpyrrole, whereas the azine is converted into a pyrrole, which closely resembles 3-acetyl-2 : 4-dimethylpyrrole, but differs from it in giving a picrate of much lower m. p. (Fischer and Bartholomäus, this vol., i, 50). With the object of discovering the cause of this difference in the behaviour, the authors have investigated the behaviour of the azines of 2-acetylpyrrole and 3-acetyl-2 : 4-dimethylpyrrole towards sodium methoxide and sodium ethoxide respectively, and find that with the azines the original acetyl group is not reduced to the ethyl group as in the case of the hydrazones, but is removed from the molecule, the further action of the alkyloxide resulting in the introduction of an alkyl group in the 1-position.

The *azine* of 2-acetylpyrrole, $C_{12}H_{14}N_4$, prepared by boiling the pyrrole compound with hydrazine hydrate, crystallises in colourless, prismatic columns, m. p. 213° (corr.), and is converted by methyl-alcoholic sodium methoxide at 200—210° into 2-methylpyrrole.

The azine of 3-acetyl-2 : 4-dimethylpyrrole when heated with alcoholic sodium ethoxide yields 3 : 5-dimethyl-2-ethylpyrrole (Abstr., 1911, i, 1019). F. B.

Action of Sodium Ethoxide on Pyrrole Derivatives. II. HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1912, 80, 6—16. Compare the vol., i, 384).—By the action of sodium ethoxide on trimethylpyrrole, crystalline tetramethylpyrrole has been obtained. In a similar manner with sodium propoxide, trimethylpropylpyrrole is formed, and has been isolated as picrate. A methylpropylpyrrole is stated by Marchlewski to be present in the hæmopyrrole mixture, but, on heating this with sodium methoxide, phyllopyrrole is practically the only product. This serves to negative Marchlewski's supposition.

When ethyl 2 : 5-dimethylpyrrole-3-carboxylate is heated with sodium ethoxide, the carbethoxy-group is eliminated. Similarly, from acetyldimethylpyrrole, dimethylpyrrole is obtained; this yields a characteristic crystalline picrate. When 2 : 4-dimethyl-5-ethylpyrrole is heated with sodium methoxide, the ethyl group in position 5 is replaced by methyl, and tetramethylpyrrole is obtained.

Methyl groups render the pyrrole nucleus unstable, dimethyl- and trimethyl-pyrrole being more sensitive than pyrrole. Acetyltrimethylpyrrole is stable; trimethylethylpyrrole is most unstable. The pyrrolecarboxylic acids are stable when pure.

The 2-azo-dyes of the pyrroles are similarly rendered more stable by the introduction of the acetyl or carboxyl group.

The picrates of the pyrroles are conveniently decomposed by shaking the suspension in ether with 25% hydrochloric acid.

2 : 3 : 4 : 5-Tetramethylpyrrole, $NH<\begin{matrix}CMe:CMe\\ \vert \\ CMe:CMe\end{matrix}$ (compare Ciamician and Silber, this vol., i, 537), crystallises in colourless platelets, m. p. 111—112°; it has an odour like naphthalene. The yellow picrate has m. p. 127—128°.

2 : 4 : 5-*Trimethyl-3-propylpyrrole*, $NH<\begin{matrix}CMe:CPr\\ \vert \\ CMe:CMe\end{matrix}$, was isolated as *picrate*, m. p. 80—91°.

2 : 4-*Dimethylpyrrole picrate* has m. p. 92—93°. E. F. A.

Conversion of Dihydrofurandicarboxylic Acid into Hydroxypyridinecarboxylic Acid. EMIL FISCHER, KURT HESS, and ALEX. STAHLSCHMIDT (*Ber.*, 1912, 45, 2456—2467).—When 2 : 5-dihydrofuran-2 : 5-dicarboxylic acid, obtained from dehydromucic acid on reduction with sodium amalgam (Hill and Wheeler, Abstr., 1901, i, 556), is heated with aqueous ammonia in presence of ammonium bromide at 160°, 2-hydroxypyridine-6-carboxylic acid,

$$CH<\begin{matrix}CH—C(OH)\\ CH:C(CO_2H)\end{matrix}>N,$$

is formed.

When further heated this compound loses carbon dioxide, forming 2-hydroxypyridine. Phosphorus pentachloride converts it into a

chloropyridinecarboxylic acid, which is reduced by hydrogen iodide to picolinic acid.

The transformation from the furan to the pyridine ring takes place in several stages. When the heating is effected in the absence of ammonium bromide at 150°, dihydrofurandicarboxylic acid is converted into the half amide; this could not be transformed into hydroxypyridinecarboxylic acid.

α-Dihydrofurandicarboxylamide is prepared by the action of ammonia on the dichloride; here, also, dehydrating agents other than ammonia were without effect.

2 : 3-Dihydrofuran-2 : 5-dicarboxylic acid, which is obtained from the 2 : 5-isomeride on boiling with alkali, is readily converted by ammonia into the same hydroxypyridinecarboxylic acid.

2-*Hydroxypyridine*-6-*carboxylic acid* forms long, thin prisms or needles, which sinter at 275° (corr.), m. p. 282° (corr. decomp.). It tastes and reacts acid, and gives a yellowish-red colour with ferric chloride. The *barium* salt forms long, narrow prisms, obliquely cut and aggregated in bunches; the *calcium* salt crystallises in microscopic, prismatic needles; the *copper* salt forms microscopic, obliquely cut prisms.

2-*Chloropyridine*-6-*carboxylic acid* crystallises in colourless platelets, which sinter at 180° (corr.), m. p. 190° (corr.). The *copper* salt $+ 4H_2O$ forms pale-coloured, microscopic columns; the *silver* salt appears as very slender, microscopic, thread-like needles; the *calcium* salt $+ H_2O$ forms short, interlaced, pointed needles.

The *monoamide* of 2 : 5-dihydrofuran-2 : 5-dicarboxylic acid,

$$C_4H_4O(CO_2H){\cdot}CO{\cdot}NH_2,$$

crystallises in microscopic prisms, m. p. 244° (corr., decomp.).

2 : 5-*Dihydrofuran*-2 : 5-*dicarboxyl chloride*, $C_4H_4O(COCl)_2$, is a colourless, strongly refractive, mobile oil of powerful odour, b. p. 146°/28 mm., which darkens in colour on keeping.

2 : 5-*Dihydrofuran*-2 : 5-*dicarboxylamide* forms colourless, stunted crystals, mostly plates, m. p. 211—212° (corr.). E. F. A.

1 : 5-Naphthylenediamine. CHEMISCHE FABRIK R. SCHEUBLE & Co. (*Chem. Zeit.*, 1912, **36**, 1226).—The unpleasant properties attributed to 1 : 5-diacetylnaphthylenediamine by Kunckell and Schneider (this vol., i, 811) are ascribed to chloroacetyl chloride and bromoacetyl chloride, each of which can cause an inflammation of the skin. Susceptibility to the action of these substances appears to be largely a personal matter, whilst persons who have recovered from one attack appear to be subsequently immune. In reply to this criticism, FRANZ KUNCKELL (*ibid.*, 1226—1227) points out that chloroacetyl chloride was employed during two years in his laboratory without unpleasant consequences. The latter were only observed when 1 : 5-naphthylenediamine was acetylated, and, since the amine itself is apparently harmless, they must be attributed to 1 : 5-diacetylnaphthylenediamine. H. W.

Ditertiary Hydrazines and Bivalent Nitrogen. HEINRICH WIELAND (*Annalen*, 1912, **392**, 127—133).—Tetraphenylhydrazine

and its homologues, analogously to hexaphenylethane, dissociate in solution into radicles, NAr_2 (Abstr., 1911, i, 570). The author's aims in the following papers are to trace as fully as possible the analogy between carbon and nitrogen as regards the existence of free radicles, and to examine the dependence of the stability of the hydrazine on the character of the substituting aryl groups. Confining the comparison to tetra-arylated hydrazines, it is found that the dissociability increases with the presence of positive groups. On the other hand, mixed dialkyldiarylhydrazines have been prepared, and are found to dissociate less readily than tetra-arylhydrazines.

C. S.

Aromatic Hydrazines. XI. Dissociation of Tetrazens. HEINRICH WIELAND and H. FRESSEL (*Annalen*, 1912, **392**, 133—156).—Franzen and Zimmermann's observations regarding the conversion of tetrazens into ditertiary hydrazines (Abstr., 1906, i, 702) require amplification. Many tetrazens require boiling for some time for the complete expulsion of the azo-nitrogen, and the products are secondary amines and Schiff's bases, doubtless formed by the interaction of the NR_2 groups, which are intermediate products. Tetraethyltetrazen, which in the pure condition is a pleasantly odorous liquid, b. p. 79°/12 mm., decomposes when heated for some time under the ordinary pressure, and yields nitrogen, diethylamine, and ethyl ethylideneamine. The formation of NEt_2 groups during the decomposition of the tetrazen is shown by passing a slow current of nitric oxide over the decomposing tetrazen, whereby nitrosodiethylamine is produced. *N*-Azopiperidine decomposes when heated for some time, and yields piperidine and tetrahydropyridine (?). It reacts with ethereal methyl iodide (3 mols.) to form dimethylpiperidinium iodide and an amorphous substance.

Tetrabenzyltetrazen is best obtained by oxidising a cold saturated alcoholic solution of *as*-dibenzylhydrazine with alcoholic *p*-benzoquinone at 0°. By being heated for six hours in boiling xylene, it yields dibenzylamine and benzylbenzylideneamine, whilst when heated with methyl iodide in benzene, it yields, amongst other products, *dibenzyldimethylammonium iodide*, m. p. 191°.

aβ-Diphenyl-aβ-dimethylhydrazine, NPhMe·NPhMe, b. p. 138°/1 mm., is obtained, together with methylaniline and the Schiff base, by heating diphenyldimethyltetrazen in boiling xylene for one and a-half hours in an atmosphere of carbon dioxide. The dissociation of the hydrazine into NPhMe can be indicated, either by distillation in a vacuum, whereby methylaniline and polymerisation products of methyleneaniline are obtained, or by heating the substance in boiling xylene in a current of nitric oxide, whereby phenylmethylnitrosoamine is produced. Diphenyldimethylhydrazine behaves towards acids like its tetrazen (of course, nitrogen is not evolved); specially characteristic is the action of slightly warmed glacial acetic acid, which produces a violet coloration, changing to blue and green. *aβ-Diphenyl-aβ-diethylhydrazine*, b. p. 141°/1 mm., behaves like its methyl homologue, and is obtained in a similar manner. The formation of ammonia and

phenylcarbylamine by the decomposition of diphenyldimethyltetrazen in boiling xylene (Franzen and Zimmermann, *loc. cit.*) has not been observed by the authors. The diphenyldibenzylhydrazine described by these two investigators (*loc. cit.*) is probably a mixture of benzylaniline and benzylideneaniline.

Unsuccessful attempts have been made to prepare ditertiary hydrazines by the action of metals on secondary *N*-chloroamines.

C. S.

Aromatic Hydrazines. XII, Dissociation of Tetra-arylhydrazines and of Diarylnitrosoamines. HEINRICH WIELAND and HANS LECHER (*Annalen*, 1912, **392**, 156—169).—Rapidly in boiling xylene, or after some months in chloroform or benzene in darkness at the ordinary temperature, tetraphenylhydrazine decomposes into diphenylamine (2 mols.) and 5 : 10-diphenyldihydrophenazine (1 mol.).

s-*Diphenyldi*-p-*tolylhydrazine*, $C_6H_4Me\cdot NPh\cdot NPh\cdot C_6H_4Me$, m. p. 123°, colourless crystals, obtained by the oxidation by potassium permanganate of phenyl-*p*-tolylamine in acetone at 10—20°, decomposes in a similar manner in boiling toluene in thirty minutes, or in chloroform or benzene in darkness after three months, the products being phenyl-*p*-tolylamine and a *diphenyldimethyldihydrophenazine*, $C_{26}H_{22}N_2$, m. p. above 315°, darkening at 267°. On the contrary, tetra-*p*-tolylhydrazine can be kept in benzene in darkness for three months without appreciable change; in chloroform, however, under similar conditions, it decomposes into *p*-ditolyldihydrotolazine, m. p. 274°, not 269° (Abstr., 1908, i, 1014), and di-*p*-tolylamine.

Tetra-*p*-anisyltetrazen decomposes in boiling benzene in an atmosphere of carbon dioxide, yielding the anisazine, m. p. 292° (not 290°, *loc. cit.*), and presumably di-*p*-anisylamine.

Diarylnitrosoamines decompose in boiling xylene in an atmosphere of carbon dioxide, yielding nitric oxide and products similar to those obtained above by the decomposition of tetra-arylhydrazines and formed by the mutual interaction of the NAr_2 radicles. Thus di-*p*-tolylnitrosoamine yields di-*p*-tolylamine and *p*-ditolyldihydrotolazine; di-*p*-anisylnitrosoamine yields the anisazine and di-*p*-anisylamine; *p*-nitrodiphenylnitrosoamine yields very easily *p*-nitrodiphenylamine and 5 : 10-*di*-p-*nitrophenyldihydrophenazine*,

$$C_6H_4<\begin{matrix}N(C_6H_4\cdot NO_2)\\N(C_6H_4\cdot NO_2)\end{matrix}>C_6H_4,$$

m. p. 183°, reddish-brown substance; di-*p*-nitrophenylnitrosoamine yields di-*p*-nitrophenylamine and 2 : 4 : 4′-trinitrodiphenylamine; *N*-nitrosocarbazole yields carbazole and 3-nitrocarbazole. In the last two cases the expected azines have not been obtained, but nitrated amines produced by some obscure reaction.

The dissociation of nitrosoamines, $NR_2\cdot NO$, by heat depends on the nature of R. No dissociation occurs when R is an alkyl group, dialkylnitrosoamines volatilising without decomposition. When R is an aryl group, the dissociation proceeds the more easily the more positive is the aromatic group.

C. S.

Aromatic Hydrazines. XIII. Some New Ditertiary Hydrazines and Tetrazens of the Aromatic Series. HEINRICH WIELAND and A. SÜSSER (*Annalen*, 1912, 392, 169—185).—s-*Diphenyl-di*-p-*anisylhydrazine*, $OMe\cdot C_6H_4\cdot NPh\cdot NPh\cdot C_6H_4\cdot OMe$, m. p. 130° (decomp.), colourless needles, and *tetra*-o-*tolylhydrazine*, $N_2(C_6H_4Me)_4$, m. p. 112°, an unstable, amorphous powder, are obtained by oxidising *p*-methoxydiphenylamine and di-*o*-tolylamine respectively in cold acetone by powdered potassium permanganate. In accord with the generalisation that the dissociation of aromatic ditertiary hydrazines is facilitated by the presence of positive nuclei, the two preceding hydrazines dissociate very easily, the former in boiling benzene, the latter in solution at the ordinary temperature.

s-Diphenyldi-*p*-anisylhydrazine develops a rose coloration in cold glacial acetic acid; the colour changes to violet by warming, and the solution then contains *p*-methoxydiphenylamine and the *dimethoxyperazonium acetate*; the *azine*, $OMe\cdot C_6H_3<{NPh \atop NPh}>C_6H_3\cdot OMe$, corresponding with the latter, is a yellow, crystalline substance, from which, by treatment with glacial acetic and anhydrous mineral acids, azonium salts are obtained, the colours and spectra of which are very similar to those of the salts of the tetramethoxylated azine (Abstr., 1908, i, 1014).

s-Diphenyldi-*p*-anisylhydrazine, dissolved in benzene and acetone at 15°, is converted by ethereal hydrogen chloride mainly into *p*-methoxydiphenylamine and p(?)-*chloro*-p-*methoxydiphenylamine*,

$$OMe\cdot C_6H_4\cdot NH\cdot C_6H_4Cl,$$

m. p. 48·5°; in addition, the *dihydrochloride*, violet needles, of 2 : 7-*dimethoxy*-5 : 10-*di*-p-*chlorophenyldihydrophenazine*,

$$OMe\cdot C_6H_3<{N(C_6H_4Cl) \atop N(C_6H_4Cl)}>C_6H_3\cdot OMe,$$

yellow needles, decomp. 281°, darkening at 244°, is obtained.

Attempts to prepare tetranaphthylhydrazines have been unsuccessful. Doubtless the oxidation of di-β-naphthylamine in cold acetone by potassium permanganate produces the $N(C_{10}H_7)_2$ radicle; however, these combine with one another to produce, not the desired tetra-β-naphthylhydrazine, but an isomeric *substance*, $C_{40}H_{28}N_2$, m. p. 273°, colourless crystals, which is very probably *a-2-β-naphthylaminonaphthyl-di-β-naphthylamine* [*tri-β-naphthyl*-1 : 2-*naphthylenediamine*],

$$C_{10}H_7\cdot NH\cdot C_{10}H_6\cdot N(C_{10}H_7)_2.$$

It is also produced by the dissociation of di-β-naphthylnitrosoamine (preceding abstract), or of tetra-β-naphthyltetrazen, or by the interaction of ethereal di-β-naphthylamine, alcoholic sodium ethoxide, and ethereal iodine for twelve hours; in the last case, a *di-iododinaphthylamine*, $C_{20}H_{13}NI_2$, m. p. 179°, yellow needles, is also obtained. The trinaphthylnaphthylenediamine forms a colourless *hydrochloride* with ethereal hydrogen chloride, is scarcely changed by concentrated sulphuric acid, and is not reduced by zinc dust and acetic acid.

as-*Di-β-naphthylhydrazine*, $NH_2\cdot N(C_{10}H_7)_2$, m. p. 141°, pearly leaflets, produced by the reduction of di-β-naphthylnitrosoamine by zinc dust and cold acetic acid and ether, is oxidised in acetone at −15° to *tetra-β-naphthyltetrazen*, $N(C_{10}H_7)_2\cdot N{:}N\cdot N(C_{10}H_7)_2$, decomp.

147°, unstable, yellow crystals, by saturated potassium permanganate.

[With H. FRESSEL.]—*Diphenylenehydrazine*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!N\cdot NH_2$, m. p. 147° (decomp.), colourless needles, is obtained by treating a moist ethereal soluton of *N*-nitrosocarbazole with zinc dust and glacial acetic acid in a freezing mixture. It forms a crystalline *hydrochloride* and *benzylidene* derivative, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!N\cdot N\colon CHPh$, m. p. 137°, yields usually carbazole by oxidation, but is converted in cold ether by *N*-hydrochloric acid and sodium hypochlorite into *bisdiphenylenetetrazen*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!N\cdot N\colon N\cdot N\!<\!\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, decomp. 216°, yellowish-green plates, which differs from all other tetrazens in its great stability towards acids. It is unchanged in boiling toluene by hydrogen chloride, and is only decomposed by concentrated sulphuric acid by warming; by prolonged boiling with copper powder in xylene, it yields nitrogen, carbazole, and a blue *substance*, possibly $(C_{12}H_7N)_x$. C. S.

Aromatic Hydrazines. XIV. Nitration of Tetraphenylhydrazine. Cyanoarylhydroxylamines. HEINRICH WIELAND and A. ROSEEU (*Annalen*, 1912, **392**, 186—195).—Nitrated tetraphenylhydrazines, the preparation of which is desirable for the comparative study of the stability of tetra-arylhydrazines, cannot be obtained by the direct action of nitric acid on account of the rapid fission of the tetraphenylhydrazine produced thereby. p-*Nitrotetraphenylhydrazine*, $NO_2\cdot C_6H_4\cdot NPh\cdot NPh_2$, m. p. 145°, orange-red plates, is obtained by warming powdered tetraphenylhydrazine with amyl nitrite. It is remarkably stable on account of the presence of the negative group (compare preceding abstracts), and is unchanged by not too prolonged boiling in solvents of high b. p., by ethereal hydrogen chloride, or by glacial acetic acid. It is reduced in alcoholic solution to diphenylamine and phenyl-*p*-phenylenediamine by stannous chloride and concentrated hydrochloric acid. *p*-Nitrotetraphenylhydrazine develops a violet coloration with concentrated sulphuric acid at 0°; after three hours, however, the substance is decomposed and yields diphenylamine, *p*-nitrodiphenylamine, and a *substance*, $C_{24}H_{19}O_2N_3$, m. p. 165°, orange prisms, which is apparently *p*-nitrodiphenylbenzidine,

$$NO_2\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NHPh.$$

[With S. GAMBARJAM.]—s-*Diphenyl-di*-p-*nitrophenylhydrazine*,

$$NO_2\cdot C_6H_4\cdot NPh\cdot NPh\cdot C_6H_4\cdot NO_2,$$

m. p. 168—169°, red, rhombic plates, is obtained by the action of pure nitrogen dioxide on a cold saturated solution of tetraphenylhydrazine in benzene. It resembles *p*-nitrotetraphenylhydrazine in its stability. It is reduced to phenyl-*p*-phenylenediamine by zinc and acetic acid. With cold concentrated sulphuric acid at 0°, it develops a violet coloration, but it decomposed after three hours, yielding *p*-nitrodiphenylamine, an orange-red *substance*, m. p. 211°, and mainly *di*-p-*nitrophenylbenzidine*, $NO_2\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NO_2$, m. p. 252°, red crystals with blue reflex.

β-Cyano-β-phenylhydroxylamine, CN·NPh·OH, obtained from β-phenylhydroxylamine and cyanogen bromide in the presence of sodium hydrogen carbonate (Abstr., 1904, i, 628), is extremely unstable, but can be isolated for a few minutes in crystalline leaflets. It dissolves in alkalis, but is insoluble in aqueous acids; ethereal hydrogen chloride produces after some time a crystalline *iminochloride hydrochloride*, OH·NPh·CCl:NH,HCl, from an aqueous solution of which at 50° the cyanophenylhydroxylamine is recovered. Hydrogen cyanide, aniline, and phenylcyanamide are formed by reducing a cold concentrated aqueous solution of this hydrochloride with stannous chloride and hydrochloric acid.

β-Cyano-β-p-tolylhydroxylamine, $C_6H_4Me\cdot N(CN)\cdot OH$, obtained in a similar manner, is likewise extremely unstable, and forms an *iminochloride hydrochloride*, C_8H_9ONCl,HCl, decomp. 155°. C. S.

Ditertiary Hydrazines. XV. Tetra-anisylhydrazine. HEINRICH WIELAND and HANS LECHER (*Ber.*, 1912, 45, 2600—2605. Compare Abstr., 1908, i, 1014).—*Tetra-anisylhydrazine*,

$$N_2(C_6H_4\cdot OMe)_4,$$

is obtained by the oxidation of dianisylamine with lead dioxide in ethereal solution at the ordinary temperature. It forms almost colourless, stellar aggregates of prisms, m. p. 90·5°, which slowly decompose when kept, and dissolves in concentrated sulphuric acid with a dark blue coloration. The union of the nitrogen atoms is so feeble that dissociation into the free radicle, $\cdot N(C_6H_4\cdot OMe)_2$, takes place in organic solvents, even at the ordinary temperature. Its solution in benzene has a light green colour, which becomes deeper on warming, owing to the greater dissociation.

With hydrochloric, sulphuric, and acetic acids, it forms dark blue quinonoid *salts*, $\begin{matrix}(OMe\cdot C_6H_4)_2N \\ OMe\cdot C_6H_4\end{matrix}\!\!>\!NX\!:\!C_6H_4\!<\!\!\begin{matrix}H \\ OMe\end{matrix}$, which, however, are very unstable and readily undergo decomposition.

The *acetate*, obtained by dissolving the hydrazine in glacial acetic acid, decomposes into dianisylamine and anisazonium acetate (Abstr., 1908, i, 1014). Further evidence of the dissociation of the hydrazine in solution is supplied by the behaviour of the compound toward nitric oxide and triphenylmethyl, with which it combines very readily in benzene solution at the ordinary temperature, yielding dianisylnitrosoamine and *ω-dianisylaminotriphenylmethane*,

$$CPh_3\cdot N(C_6H_4\cdot OMe)_2.$$

The last-mentioned substance crystallises in colourless prisms, which melt at 156° to a red liquid, and dissociates much less readily than the analogously constituted compounds previously described.

In benzene or acetone solution, the hydrazine decomposes in the course of a few hours at the ordinary temperature into dianisylamine and anisazine. F. B.

Reductions in the Glyoxaline Series. I. Reduction of Diphenylglyoxalone. HEINRICH BILTZ (*Annalen*, 1912, 391, 169—190).—4:5-Diphenylglyoxalone is not reduced by zinc and boiling acetic and hydrochloric acids, hydriodic acid and phosphorus

at 180°, aqueous alcoholic sodium stannite, or sodium and absolute alcohol at 40°. At the b. p., however, the last reagent produces 4 : 5-*diphenyl*-4 : 5-*dihydroglyoxalone*, $\begin{matrix}\text{CHPh}\cdot\text{NH}\\ |\\ \text{CHPh}\cdot\text{NH}\end{matrix}\!\!>\!\text{CO}$, m. p. 292—293°, together with a little of an *isomeride*, m. p. 245—246°. Diphenyldihydroglyoxalone does not react with bromine or potassium permanganate, forms a *diacetyl* derivative, m. p. 160°, yields dibenzoylcarbamide by energetic treatment with chromic acid, and is partly converted into *meso*-$\alpha\beta$-diphenylethylenediamine (following abstract) by hydrogen bromide in acetic acid.

The by-product, m. p. 245—246°, cannot be converted into the isomeride. It contains the glyoxaline skeleton, and in its behaviour corresponds with the formula, $\begin{matrix}\text{CHPh}\cdot\text{NH}\\ |\\ \text{CPh}{=\!=\!=}\text{N}\end{matrix}\!\!>\!\text{CH}\cdot\text{OH}$, of 2-*hydroxy*-4 : 5-*diphenyl*-2 : 5-*dihydroglyoxaline*, being produced probably by the reduction of the enolic modification of the diphenylglyoxalone. It forms a *diacetyl* derivative, m. p. 190—191°, from which an *acetyl* derivative, $C_{17}H_{16}O_2N_2$, m. p. 209—210°, is obtained by careful hydrolysis with aqueous alcoholic ammonia; both derivatives yield the hydroxydiphenyldihydroglyoxaline by treatment with alcoholic potassium hydroxide. Hydroxydiphenyldihydroglyoxaline is unsaturated. With bromine in chloroform, it forms an unstable orange-red *perbromide*, from which an unstable *dibromide*, $C_{15}H_{14}ON_2Br_2$, is produced; by warming or by treatment with alcohol, the dibromide is re-converted into the hydroxydiphenyldihydroglyoxaline. The latter is changed to 4 : 5-diphenylglyoxalone by bromine in boiling alcohol.

The action of hydrogen bromide on 2-hydroxy-4 : 5-diphenyl-2 : 5-dihydroglyoxaline in boiling chloroform yields 3-*bromo*-2-*hydroxy*-4 : 5-*diphenyltetrahydroglyoxaline*, $\begin{matrix}\text{CHPh-NH}\\ |\\ \text{CHPh}\cdot\text{NBr}\end{matrix}\!\!>\!\text{CH}\cdot\text{OH}$, which easily loses hydrogen bromide by warming or treatment with alcohol By boiling with hydrogen bromide in glacial acetic acid, the preceding bromide or hydroxydiphenyldihydroglyoxaline itself is converted into the hydrobromide of *meso*-$\alpha\beta$-diphenylethylenediamine.

The oxidation by solid potassium permanganate of hydroxydiphenyl dihydroglyoxaline in aqueous acetone yields dibenzoylcarbamide.

C. S.

Reductions in the Glyoxaline Series. II. Reduction of Thioldiphenylglyoxalone. HEINRICH BILTZ and PAUL KREBS (*Annalen*, 1912, **391**, 191—214).—2-Thiol-4 : 5-diphenylglyoxaline is obtained very conveniently by heating benzoin and thiocarbamide at 200°. It cannot be acetylated, and is converted almost quantitatively into benzil by alcohol and bromine.

Unlike the corresponding diphenylglyoxaline (preceding abstract), thiol-4 : 5-diphenylglyoxaline yields only one product by reduction with sodium and boiling absolute alcohol. The position of the two hydrogen atoms taken up has not been ascertained beyond doubt. However, since the general behaviour of thioldiphenylglyoxaline corresponds with that of the enolic modification, the reduction product is most

probably 2-*thiol*-4 : 5-*diphenyl*-2 : 5-*dihydroglyoxaline*,

$$\begin{array}{l}CHPh\cdot NH \\ CPh{:}N\end{array}\!\!>\!CH\cdot SH.$$

It has m. p. 315°, and behaves like a mercaptan. Thus it dissolves in 10% sodium hydroxide, and forms a *sodium* salt, $C_{15}H_{13}N_2SNa$, large leaflets. With boiling alcohol and ethyl iodide, it yields the *hydriodide*, m. p. 245°, of the *ethyl ether*, $C_{17}H_{18}N_2S$, m. p. 186°, colourless needles.

Attempts to replace the sulphur by oxygen and thus to produce 2-hydroxy-4 : 5-diphenyl-2 : 5-dihydroglyoxaline (preceding abstract) have not been successful. It is converted by alcohol and bromine water into benzil, and by boiling 3% nitric acid into 4 : 5-diphenylglyoxaline. When oxidised by alkaline potassium permanganate, it yields 4 : 5-diphenylglyoxaline-2-sulphonic acid.

By reduction with sodium and boiling amyl alcohol, thioldiphenyldihydroglyoxaline is converted into *meso*-$\alpha\beta$-diphenylethylenediamine. The *hydrochloride*, m. p. 256° (decomp.), *platinichloride*, m. p. 265° (decomp.), and *dibenzoyl* derivative, m. p. 350°, of this base, and the *hydrochloride*, m. p. 251° (decomp.), *disalicylidene* derivative, m. p. 200—201°, and dibenzoyl derivative, m. p. 287°, of the racemic modification, are described, since the literature of these two bases is in many points erroneous. C. S.

Reductions in the Glyoxaline Series. III. Reduction of Diphenylglyoxaline and Triphenylglyoxaline. HEINRICH BILTZ and PAUL KREBS (*Annalen*, 1912, 391, 210—214).—Kohler has described (*Diss.*, Erlangen, 1887) a triphenyldihydroglyoxaline, m. p. 257°, which he obtained by the action of sodium and alcohol on lophine (2 : 4 : 5-triphenylglyoxaline). It is now shown that this substance is only impure lophine; by crystallisation from absolute alcohol, pyridine, or ether, the m. p. is raised to that of lophine, 275°. Lophine is not reduced by sodium and boiling amyl alcohol. The same is true of 4 : 5-diphenylglyoxaline; the product, after crystallisation from alcohol, has a constant m. p. about 216°. It is, however, only impure 4 : 5-diphenylglyoxaline; the impurities can be removed by purification through the hydrochloride, and the substance then has the correct m. p., 227°. C. S.

Reductions in the Glyoxaline Series. IV. Reduction of Thiodiphenylhydantoin. HEINRICH BILTZ and KARL SEYDEL (*Annalen*, 1912, 391, 215—230).—5 : 5-Diphenylhydantoin and thio-5 : 5-diphenylhydantoin are extremely resistant to the attack of many reducing agents. The latter, however, is converted by sodium and boiling amyl alcohol into 5 : 5-*diphenyltetrahydro*-4-*glyoxalone*, $\begin{array}{l}CPh_2\cdot NH \\ CO—NH\end{array}\!\!>\!CH_2$, m. p. 185·5—186·5°, which is purified through the *hydrochloride*, decomp. 205—206°. This product is isomeric with the 4 : 5-diphenyldihydroglyoxalones (preceding abstracts), but differs from them in its pronounced basic character (*nitrate*, decomp. 171°; *picrate*, m. p. about 158°). By energetic oxidation it yields benzophenone, but is converted by treatment with potassium permanganate, in $2N$-nitric acid or glacial acetic acid at 60°, or suspended in sodium

hydroxide at 70—80°, into 5 : 5-*diphenyl*-4 ; 5-*dihydro*-4-*glyoxalone*, $\begin{array}{l}CPh_2\cdot NH \\ | \\ CO\text{——}N\end{array}\!\!>CH$, m. p. 166—167°. This substance, which is re-converted into its generator by zinc and boiling dilute hydrochloric acid, is amphoteric, being soluble in sodium hydroxide and forming salts with strong, inorganic acids (*hydrochloride*, m. p. 264° [decomp.]; *nitrate*, m. p. 170—171° [decomp.]). It forms an *acetyl* derivative, m. p. 138—139°, and 1-*methyl* derivative, m. p. 175—176°, and is converted into ammonia and *aminodiphenylacetic acid*, $NH_2\cdot CPh_2\cdot CO_2H$, m. p. 245—246° (decomp.), by prolonged boiling with 20% sodium hydroxide. Similarly, the 1-methyl derivative is decomposed into ammonia and *methylaminodiphenylacetic acid*, $NHMe\cdot CPh_2\cdot CO_2H$, m. p. 211° (decomp.), by boiling alcohol and 33% potassium hydroxide. This decomposition proves that in 5 : 5-diphenyl-1-methyl-4 : 5-dihydroglyoxal-4-one the methyl group is in position-1 and the double linking in the position 2 : 3.

When 5 : 5-diphenyl-4 : 5-dihydro-4-glyoxalone is boiled with water, it is converted into 2-*hydroxy*-5 : 5-*diphenyltetrahydro*-4-*glyoxalone*, $\begin{array}{l}CPh_2\cdot NH \\ | \\ CO\text{—}NH\end{array}\!\!>CH\cdot OH$, m. p. 165° (decomp.), which is also obtained as a by-product in the action of alkaline potassium permanganate on 5 : 5-diphenyltetrahydro-4-glyoxalone. At 170° it loses water and is re-converted into 5 : 5-diphenyl-4 : 5-dihydro-4-glyoxalone. In a similar manner, boiling water converts 1-acetyl-5 : 5-diphenyl-4 : 5-dihydro-4-glyoxalone into 1-*acetyl*-2-*hydroxy*-5 : 5-*diphenyltetrahydro*-4-*glyoxalone*, m. p. 207° (decomp.). C. S.

Reductions in the Glyoxaline Series. V. Influence of Substituents on the Acidity of Imino-groups. HEINRICH BILTZ (*Annalen*, 1912, **391**, 231—234. Compare preceding abstracts).—The influence of neighbouring substituents on the acidity of the imino-group is well illustrated by the preceding examples. 5 : 5-Diphenylhydantoin is strongly acidic. 5 : 5-Diphenyltetrahydro-4-glyoxalone is a pronounced, but not a strong, base. 2-Hydroxy-4 : 5-diphenyl-2 : 5-dihydroglyoxaline, 2-hydroxy-5 : 5-diphenyltetrahydro-4-glyoxalone, and 4 : 5-diphenyl-4 : 5-dihydroglyoxalone are neutral substances. 4 : 5-Diphenylglyoxalone has a feebly acid character; 5 : 5-diphenyl-3-methylhydantoin is rather more acidic, and 5 : 5-diphenyl-4 : 5-dihydro-4-glyoxalone is still more so.

Glyoxaline, 4 : 5-dihydroglyoxaline, and their alkyl derivatives are pronounced bases. Strongly acidic substituents in positions 4 and 5 render 4 : 5-dihydroglyoxaline amphoteric. Glyoxalones are neutral or very feebly amphoteric. C. S.

Pyrimidines. LVI. Action of Hydroxylamine on 4-Methyl-1 : 6-dihydro-6-pyrimidone-2-thioloxalylacetic Acid. α-Oximino-β-thiolpropionic Acid. TREAT B. JOHNSON and NORMAN A. SHEPARD (*Amer. Chem. J.*, 1912, **48**, 279—296).—Piutti (Abstr., 1888, 677) has effected the synthesis of aspartic acid by reducing the

oxime of ethyl oxalacetate with sodium amalgam and hydrolysing the product. The present investigation was undertaken in order to ascertain whether the unknown aminothiolsuccinic acid,

$$CO_2H\cdot CH(SH)\cdot CH(NH_2)\cdot CO_2H,$$

could be obtained by the action of hydroxylamine on a thiol derivative of ethyl oxalacetate.

When ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thioloxalylacetate (Abstr., 1911, i, 925) is dissolved in strong hydrochloric acid and the solution evaporated to dryness, 4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*-2-*thiolpyruvic acid*, $NH<\begin{matrix}C(S\cdot CH_2\cdot CO\cdot CO_2H):N\\CO\text{———————}CH\end{matrix}>CMe$, m. p. 210—212° (decomp.), is produced, which forms hexagonal prisms. If, however, the solution of the ethyl ester in hydrochloric acid is warmed, ethyl chloride is evolved, and, on evaporating the solution nearly to dryness, 4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*-2-*thioloxalacetic acid*, $NH<\begin{matrix}C[S\cdot CH(CO\cdot CO_2H)\cdot CO_2H]:N\\CO\text{————————}CH\end{matrix}>CMe$, m. p. 159—161° (decomp.), is obtained, which crystallises in slender prisms. When the diethyl ester is heated with potassium hydroxide solution, it is converted into ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate (*loc. cit.*).

By the action of hydroxylamine on 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thioloxalacetic acid, three compounds are produced. The primary product of the reaction seems to be 4-methyl-1 : 6-dihydro-6-pyrimidone-2-oximinothiolsuccinic acid,

$$NH<\begin{matrix}C[S\cdot CH(C(:NOH)\cdot CO_2H)\cdot CO_2H]:N\\CO\text{——————————}CH\end{matrix}>CMe,$$

but this could not be isolated, although its *sodium* salt was prepared; the acid is unstable and evolves carbon dioxide at the ordinary temperature with formation of 4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*-2-*oximinothiolpropionic acid*, $NH<\begin{matrix}C[S\cdot CH_2\cdot C(:NOH)\cdot CO_2H]:N\\CO\text{————————}CH\end{matrix}>CMe$, m. p. 160—161° (decomp.), which crystallises in prisms. Another product of the reaction is 2-*oximino*-4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*,

$$NH<\begin{matrix}C(:NOH)\cdot NH\\CO\text{———}CH\end{matrix}>CMe,\tfrac{1}{2}H_2O,$$

m. p. 225—228° (decomp.), which forms stout blocks or prisms. The third product of the reaction is *a-oximino-β-thiolpropionic acid*, $HS\cdot CH_2\cdot C(:NOH)\cdot CO_2H$, m. p. 178—180° (decomp.), which crystallises in needles.

When 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolpyruvic acid is treated with hydroxylamine, it is converted into 2-oximino-4-methyl-1 : 6-dihydro-6-pyrimidone.

If 4-methyl-1 : 6-dihydro-6-pyrimidone-2-oximinothiolpropionic acid is reduced with stannous chloride and hydrochloric acid, 4-methyluracil is produced. Reduction with zinc dust and formic acid results in the formation of 2-thio-4-methyluracil; on treating the filtrate from this substance with benzoyl chloride, a small quantity of benzoylalanine is obtained. Reduction with aluminium amalgam yields 4-methyluracil and 2-thio-4-methyluracil.

When 2-oximino-4-methyl-1 : 6-dihydro-6-pyrimidone is reduced with

stannous chloride and hydrochloric acid, it is converted into 4-methyluracil.

The action of hydroxylamine on ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thioloxalacetate results in the formation of ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate and 2-oximino-4-methyl-1 : 6-dihydro-6-pyrimidone.

Experiments were carried out on the reduction of α-oximino-β-thiolpropionic acid, but in no case was either cysteine or cystine produced. E. G.

Pyrimidines. LVII. Action of Potassium Thiocyanate on Primary Haloids. Treat B. Johnson and Arthur J. Hill (*Amer. Chem. J.*, 1912, **48**, 296—306).—It has been shown previously (Abstr., 1908, i, 837) that by the action of potassium thiocyanate on pyrimidine imide chlorides, corresponding with the formula $\underbrace{\mathrm{N\cdot C\cdot N\cdot C{:}C\cdot C}}\mathrm{Cl}$, the final product is a thiocarbimide. In some cases, however, it was found that the primary thiocyanates could be isolated and purified. The haloid derivatives of 4- and 5-methyldiketotetrahydropyrimidines, $\mathrm{NH}{<}\begin{matrix}\mathrm{CO\cdot NH}\\\mathrm{CO{-}C}\end{matrix}{>}\mathrm{C\cdot CH_2R}$ and $\mathrm{NH}{<}\begin{matrix}\mathrm{CO{-\!-}NH}\\\mathrm{CO\cdot C(CH_2R)}\end{matrix}{>}\mathrm{C}\cdot$, should theoretically react with potassium thiocyanate to form thiocarbimides, and the present work was undertaken to test this assumption.

When the *sodium* salt of ethyl $\alpha\gamma$-diphenoxyacetoacetate,

$$\mathrm{OPh\cdot CH_2\cdot CO\cdot CNa(OPh)\cdot CO_2Et},$$

is heated with an alcoholic solution of thiocarbamide, 2-*thio*-5-*phenoxy*-4-*phenoxymethyltetrahydro*-6-*pyrimidone*,

$$\mathrm{NH}{<}\begin{matrix}\mathrm{CS{-\!-}NH}\\\mathrm{CO\cdot C(OPh)}\end{matrix}{>}\mathrm{C\cdot CH_2\cdot OPh},$$

m. p. 218°, is produced, which crystallises in slender prisms. On treating this compound with ethyl iodide and sodium ethoxide, it is converted into 2-*ethylthiol*-5-*phenoxy*-4-*phenoxymethyl*-1 : 6-*dihydro*-6-*pyrimidone*, $\mathrm{NH}{<}\begin{matrix}\mathrm{C(SEt){=}N}\\\mathrm{CO\cdot C(OPh)}\end{matrix}{>}\mathrm{C\cdot CH_2\cdot OPh}$, m. p. 170°, which forms hexagonal prisms.

2 : 6-*Diketo*-5-*phenoxy*-4-*phenoxymethyltetrahydropyrimidine*,

$$\mathrm{NH}{<}\begin{matrix}\mathrm{CO{-\!-}NH}\\\mathrm{CO\cdot C(OPh)}\end{matrix}{>}\mathrm{C\cdot CH_2\cdot OPh},$$

m. p. 200°, obtained by the action of chloroacetic acid on 2-thio-5-phenoxy-4-phenoxymethyltetrahydro-6-pyrimidone, crystallises in needles, and when heated with hydrochloric acid is converted into 2 : 6-*diketo*-5-*phenoxy*-4-*chloromethyl-tetrahydropyrimidine*,

$$\mathrm{NH}{<}\begin{matrix}\mathrm{CO{-\!-}NH}\\\mathrm{CO\cdot C(OPh)}\end{matrix}{>}\mathrm{C\cdot CH_2Cl},$$

m. p. 248°, which forms square plates. If the latter substance is heated with an alcoholic solution of potassium thiocyanate, it yields 2 : 6-*diketo*-5-*phenoxy*-4-*thiolmethyltetrahydropyrimidine*,

$$\mathrm{NH}{<}\begin{matrix}\mathrm{CO{-\!-}NH}\\\mathrm{CO\cdot C(OPh)}\end{matrix}{>}\mathrm{C\cdot CH_2\cdot SH},$$

which crystallises in needles, and decomposes at 182°. The thiocyanate seems to be the primary product of the reaction, but instead

of becoming transformed into a thiocarbimide, it loses its cyanogen radicle and yields the mercaptan.

When the *sodium* salt of ethyl $\alpha\alpha$-dinaphthoxyacetoacetate is heated with an alcoholic solution of thiocarbamide, 2-*thio*-5-*naphthoxy*-4-*naphthoxymethyltetrahydro*-6-*pyrimidone*,

$$NH<\begin{matrix}CS\text{———————}NH\\CO\cdot C(O\cdot C_{10}H_7)\end{matrix}>C\cdot CH_2\cdot O\cdot C_{10}H_7,$$

m. p. 224—226°, is produced, which crystallises in rhombic plates, and when treated with ethyl bromide and sodium ethoxide is converted into 5-*naphthoxy*-2-*ethylthiol*-4-*naphthoxymethyl*-1 : 6-*dihydro*-6-*pyrimidone*, $NH<\begin{matrix}C(SEt)\text{===}N\\CO\cdot C(OC_{10}H_7)\end{matrix}>C\cdot CH_2\cdot OC_{10}H_7$, m. p. 198°, which crystallises in needles.

2 : 6-*Diketo*-5-*naphthoxy*-4-*naphthoxymethyltetrahydropyrimidine*,

$$NH<\begin{matrix}CO\text{———————}NH\\CO\cdot C(O\cdot C_{10}H_7)\end{matrix}>C\cdot CH_2\cdot O\cdot C_{10}H_7,$$

m. p. 256—258°, prepared by the action of chloroacetic acid on 2-thio-5-naphthoxy-4-naphthoxymethyltetrahydro-6-pyrimidone, forms minute needles. Attempts to convert this compound into 2 : 6-diketo-5-naphthoxy-4-chloromethyltetrahydropyrimidine were not successful.

E. G.

Pyrimidines. LVIII. Oximes of Some Thioglycollide Compounds and their Behaviour on Reduction. TREAT B. JOHNSON and ROBERT C. MORAN (*Amer. Chem. J.*, 1912, 48, 307—320).—Johnson and Shepard (this vol., i, 911) have described α-oximino-β-thiolpropionic acid and 4-methyl-1 : 6-dihydro-6-pyrimidone-2-oximinothiolpropionic acid. Attempts to reduce these substances to the corresponding amino-compounds were not successful, and the results rendered it desirable to examine another series of oximes containing the complex $HON\!:\!\overset{|}{C}\cdot CH_2\cdot S\cdot$ in order to ascertain whether the unexpected behaviour on reduction was due to the presence of the carboxyl group. An investigation has therefore been made of certain oximes containing an alkyl group in place of the carboxyl group, and it has been found that, in general, oximes of the formula

$$NH<\begin{matrix}C(S\cdot CH_2\cdot CR\!:\!NOH)\!:\!N\\CO\text{——————————}CH\end{matrix}>CMe$$

(where $R = CH_3$, C_6H_5, or CO_2H) are converted by reducing agents into amines, $NH_2\cdot CHRMe$, and 2-thio-4-methyluracil,

$$NH<\begin{matrix}CS\cdot NH\\CO\cdot CH\end{matrix}>CMe.$$

2-*Benzoylmethylthiol*-4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*,

$$NH<\begin{matrix}C(S\cdot CH_2Bz)\!:\!N\\CO\text{————————}CH\end{matrix}>CMe,$$

m. p. 175°, obtained by the action of bromoacetophenone on the sodium salt of 2-thio-4-methyluracil, crystallises in prisms; its *sodium* salt decomposes at 206°. The mother liquor from this substance yields 6-*benzoylmethoxy*-2-*benzoylmethylthiol*-4-*methylpyrimidine*,

$$N<\begin{matrix}C(S\cdot CH_2Bz)\!:\!N\text{—}\\C(O\cdot CH_2Bz)\cdot CH\end{matrix}>CMe,$$

m. p. 118—119°, which forms prismatic crystals, and on hydrolysis with concentrated hydrochloric acid is converted into 2-benzoylmethylthiol-4-methyl-1 : 6-dihydro-6-pyrimidone. The latter compound on prolonged hydrolysis yields 4-methyluracil, and on reduction with aluminium amalgam gives 2-thio-4-methyluracil.

2-*Acetylmethylthiol*-4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*,

$$NH<\begin{matrix}C(S\cdot CH_2Ac):N \\ CO\text{———}CH\end{matrix}>CMe,$$

m. p. 152°, prepared by the action of chloroacetone on the sodium salt of 2-thio-4-methyluracil, crystallises in slender needles.

The *oxime* of 3-benzoylmethylthiol-4-methyl-1 : 6-dihydro-6-pyrimidone, $NH<\begin{matrix}C(S\cdot CH_2\cdot CPh:NOH):N \\ CO\text{————}CH\end{matrix}>CMe$, m. p. 183°, forms pale yellow crystals; its *hydrochloride* was prepared. On reducing this oxime with ferrous sulphate and ammonia, formic acid and zinc dust, or sodium amalgam, 2-thio-4-methyluracil is invariably produced. In the experiment in which sodium amalgam was used, phenylethylamine was also obtained.

The *phenylhydrazone* of 2-benzoylmethylthiol-4-methyl-1 : 6-dihydro-6-pyrimidone, $NH<\begin{matrix}C(S\cdot CH_2\cdot CPh:N\cdot NHPh):N \\ CO\text{————}CH\end{matrix}>CMe$, m. p. 295°, crystallises in needles, and on reduction with sodium amalgam or aluminium amalgam yields 2-thio-4-methyluracil. E. G.

Ring Containing a Triple Linking. PAUL RUGGLI (*Annalen*, 1912, **392**, 92—100).—oo′-*Dicarbimidotolane*, $NCO\cdot C_6H_4\cdot C:C\cdot C_6H_4\cdot NCO$, m. p. 149—150·5°, almost colourless needles, obtained by passing carbonyl chloride into a suspension of dry, finely divided *oo*′-diaminotolane dihydrochloride in hot xylene, is converted by boiling alcohol into oo′-*dicarbethoxyaminotolane*, $CO_2Et\cdot NH\cdot C_6H_4\cdot C:C\cdot C_6H_4\cdot NH\cdot CO_2Et$, m. p. 134·5—135·5°, white leaflets. The action of oxalyl, malonyl, or sulphuryl chloride on *oo*′-diaminotolane does not yield crystalline products, but the interaction of *oo*′-diaminotolane and succinyl chloride in very dilute benzene solution yields, in addition to amorphous products, cyclo*succinyldiaminotolane*, $NH<\begin{matrix}CO\cdot CH_2\cdot CH_2\cdot CO \\ C_6H_4\cdot C:C\cdot C_6H_4\end{matrix}>NH$, m. p. 237—238°, colourless, felted needles. The substance cannot be diazotised, and does not respond to Lauth's test for an amino-group. It cannot be methylated by methyl sulphate, and is remarkably stable to acids and alkalis; by prolonged boiling with 33% methyl-alcoholic potassium hydroxide, it yields *oo*′-diaminotolane and succinic acid (identified by the fluorescein test). C. S.

4 : 5 : 4′ : 5′-Tetramethylindigotin. FRANZ KUNCKELL and HANNS SCHNEIDER (*J. pr. Chem.*, 1912, [ii], **86**, 429—432. Compare this vol., i, 268).—ω-*Chloro-2-acetylamino*-4 : 5-*dimethylacetophenone*,

$$CH_2Cl\cdot CO\cdot C_6H_2Me_2\cdot NHAc,$$

prepared by the interaction of chloroacetyl chloride and aceto-4-*o*-xylidide in carbon disulphide solution in the presence of aluminium chloride, forms yellowish-red, golden needles, m. p. 166—167°, and is hydrolysed by hydrochloric acid to ω-*chloro-2-amino*-4 : 5-*dimethylaceto*-

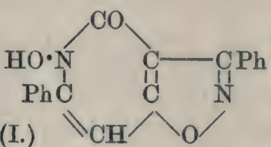
phenone hydrochloride, lustrous, green, silky needles (decomp. above 300°), from which the free *base*, having m. p. 124°, is liberated by the action of ammonium carbonate. It yields *a nitro*-derivative, crystallising in almost white needles m. p. 180°, and is converted by boiling with aqueous sodium hydroxide into 4 : 5 : 4′ : 5′-*tetramethylindigotin.*

It is also mentioned that bromopropionyl bromide reacts with aceto-4-*o*-xylidide to form a substance crystallising in greenish-yellow needles, and that *p*-acetotoluidide has been converted into 5 : 5′-*dibromo*-6 : 6′-*diacetylamino*-3 : 3′-*dimethylindigotin.* F. B.

The Action of Hydroxylamine and Phenylhydrazine on Benzoyldehydracetic Acid. JOH. SCHÖTTLE (*Ber.*, 1912, **45**, 2340—2347. Compare Petrenko-Kritschenko and Schöttle, Abstr., 1911, i, 1020; also this vol., i, 128).—When a mixture of benzoyldehydracetic acid or its phenyl-lactam with excess of hydroxylamine hydrochloride and potassium hydroxide is kept at room temperature for a week, an acidic substance,

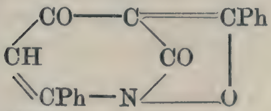
$$\mathrm{CPh}{<}\begin{matrix}\mathrm{CH}\text{———}\mathrm{CO}\\ \mathrm{N(OH)}\text{—}\mathrm{CO}\end{matrix}{>}\mathrm{CH{\cdot}CPh{:}NOH},$$

m. p. 151—152° (decomp.), is obtained; the *silver* salt was isolated. If, however, an aqueous alcoholic solution of the same substances without the potassium hydroxide is warmed on the water-bath for three to four hours, three molecules of water are eliminated, with the formation of a crystalline acidic substance, m. p. 193° (decomp.), to which is attributed the annexed formula (I); this gives a deep blue coloration with ferric chloride; the *potassium* salt, m. p. 232—233° (decomp.), and *silver* salts were prepared, also the *acetyl* derivative, m. p. 178°. In the preparation of the above substance (I.) there is obtained a small quantity of a substance (formula II), needles, m. p. 218°. The structure given in formula (I) is confirmed by the action of alcoholic potassium hydroxide, which gives rise to a *substance*,



(I.)

$$\mathrm{CO}{<}\begin{matrix}\mathrm{CH{:}CPh}\\ \mathrm{CH_2{\cdot}CO}\end{matrix}{>}\mathrm{N{\cdot}OH},$$



(II.)

needles, m. p. 182—183°; the *silver* salt and unstable *acetyl* derivative were isolated. Hydrolysis of substance (I) with hydrochloric acid at 193° in a sealed tube produced 3-*phenyl*-5-*phenacyl*iso*oxazole*, $\begin{matrix}\mathrm{CPh}\text{—}\mathrm{CH}\\ \mathrm{N}\text{———}\mathrm{O}\end{matrix}{>}\mathrm{CH_2{\cdot}COPh}$, m. p. 90°, which gives an *oxime*, m. p. 148°, and can be oxidised in alkaline acetone solution by permanganate to 3-*phenyl*iso*oxazole*-5-*carboxylic acid*, $\begin{matrix}\mathrm{CPh{\cdot}CH}\\ \mathrm{N}\text{———}\mathrm{O}\end{matrix}{>}\mathrm{C{\cdot}CO_2H}$, m. p. 177—178°, and benzoic acid.

The action of phenylhydrazine hydrochloride on benzoyldehydracetic acid or its phenyl-lactam in alcoholic solution gives as product a very stable *substance*, m. p. 268°, of which the constitution is uncertain. D. F. T.

Aromatic Carbamides. A. KRAMMER (*J. pr Chem.*, 1912, [ii], 86, 359—366).—p-*Anilinophenylcarbamide*,

$$NHPh \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2,$$

prepared by the interaction of *p*-aminodiphenylamine and potassium cyanate in aqueous solution, has m. p. 201°, and yields a reddish-violet *bromo*-derivative, $C_{13}H_{12}ON_3Br$, m. p. 163°. When heated with aromatic amines it forms substituted carbamides of the general formula $NHPh \cdot C_6H_4 \cdot NH \cdot CO \cdot NHR$. The following compounds were prepared in this manner: p-*anilinodiphenylcarbamide*, a reddish-violet, microcrystalline substance, m. p. 213·5° ; p-*anilino*-o-*tolylcarbamide* ($R = \cdot C_6H_4Me$), m. p. 234°; p-*anilino*-m-*tolylcarbamide*, m. p. 226°; p-*anilino*-p-*tolylcarbamide*, m. p. 231°, which forms a greenish-yellow *nitroso*-derivative, $NHPh \cdot C_6H_4 \cdot NH \cdot CO \cdot N(NO) \cdot C_6H_4Me$, m. p. 190°; p-*anilinophenyl*-o-*nitrophenylcarbamide* ($R = \cdot C_6H_4 \cdot NO_2$) has m. p. 178°, and is also obtained by nitrating *p*-anilinodiphenylcarbamide; p-*anilinophenyl*-4-*nitro*-o-*tolylcarbamide*

$$(R = \cdot C_6H_3Me \cdot NO_2),$$

m. p. 184°; p-*anilinophenyl*-3-*nitro*-p-*tolylcarbamide*, m. p. 181°. The nitro-compounds have a brown colour, whilst the unsubstituted tolyl compounds are reddish-violet to bluish-violet. F. B.

Simplest Indophenols and Indamines. GUSTAV HELLER (*Annalen*, 1912, 392, 16—48).—Substances of the type

$$NH{:}C_6H_4{:}N \cdot C_6H_4 \cdot OH$$

are usually classified as indophenols. The author classifies all dyes containing $O{:}C_6H_4{:}N\cdot$ as indophenols and all dyes containing $NH{:}C_6H_4{:}N\cdot$ as indamines.

In 33% sodium hydroxide at −10°, phenol and *p*-aminophenol are oxidised by sodium hypochlorite (D.R.-P. 157288), yielding the *sodium* salt, blue leaflets, of the *indophenol*, $O{:}C_6H_4{:}N \cdot C_6H_4 \cdot OH$, m. p. 160° (decomp.), which crystallises from benzene in red needles and from petroleum in brown leaflets. The *acetyl* derivative, m. p. 115—116°, forms clusters of red needles. The indophenol is remarkably stable to sulphuric acid stronger than 70%; it yields *p*-benzoquinone by treatment with warm dilute hydrochloric acid, but is converted by concentrated hydrochloric acid into quinol and *p*-benzoquinoneimine; the latter, however, reacts with some unchanged indophenol to form a complex *substance*, m. p. above 310°, violet leaflets.

By treatment with primary aromatic amines in cold alcohol and acetic acid, the sodium derivative of indophenol yields *dianilino*-derivatives of the type $O{:}C_6H_4{:}N \cdot C \genfrac{}{}{0pt}{}{<C(NHAr){:}CH>}{<CH \cdot C(NHAr)>} C \cdot OH$. Thus aniline yields $C_{24}H_{19}O_2N_3$, m. p. 210°, brown needles (*acetyl* derivative, m. p. 197°); *p*-toluidine yields $C_{26}H_{23}O_2N_3$, m. p. 250°; *o*-toluidine yields

$$C_{26}H_{23}O_2N_3,$$

m. p. 227—240° (decomp.), green needles; 2-*m*-xylidine yields $C_{28}H_{27}O_2N_3$, m. p. 280°, dark brown needles; acetyl-*p*-phenylenediamine yields $C_{28}H_{25}O_4N_5$, m. p. 285°, violet-brown needles. By oxidation with chromic acid, these dianilino-derivatives in alcohol and acetic acid at 60° are converted into the corresponding dianils; *dianiloindophenol*, $O{:}C_6H_4{:}N \cdot C \genfrac{}{}{0pt}{}{<C({:}NPh) \cdot CH>}{<CH \cdot C({:}NPh)>} C \cdot OH$, decomp. 235—242°, red needles;

di-o-*toluidoindophenol*, $C_{26}H_{21}O_2N_3$, decomp. 245°, red needles; *di*-p-*acetylaminoaniloindophenol*, m. p. above 300°; *di*-2-m-*xylidoindophenol*, $C_{28}H_{25}O_2N_3$, darkening at 225°, flat plates.

These dianilo-derivatives are stable to acids, but are converted by boiling alcoholic potassium hydroxide into arylated safranols. The conversion might occur in two ways; for example, dianiloindophenol can be transformed into $NHPh\cdot C_6H_2(OH)<\overset{N}{\underset{NPh}{}}>C_6H_3{:}O$ or

$$NPh{:}C_6H_2(OH)<\overset{N}{\underset{N(C_6H_4\cdot OH)}{}}>C_6H_4.$$

The former constitution is accepted; the transformation represented by the latter formula should be impossible with the di-*m*-xylidoindophenol, whereas, actually, a safranol is obtained in this case.

The substances are characterised as safranols by their great stability, resistance to reduction, and the green coloration with concentrated sulphuric or hydrochloric acid. 7-Anilinosafranol, m. p. above 285°, red needles, is identical with Fischer and Hepp's anilinosafranol (Abstr., 1895, i, 608; 1896, i, 323), and is converted into their dihydroxy*apo*safranol (7-hydroxysafranol) by 30% sulphuric acid at 180—185°. 7-o-*Toluidino*-10-o-*tolylsafranol*,

$$C_6H_4Me\cdot NH\cdot C_6H_2(OH)<\overset{N}{\underset{N(C_7H_7)}{}}>C_6H_3{:}O,$$

decomp. 265°, separates from alcohol in dark red, flattened, triclinic crystals containing 2EtOH, and is converted by 25% sulphuric acid at 170—175° into 7-*hydroxy*-10-o-*tolylsafranol*, $C_{19}H_{14}O_3N_2$, reddish-brown crystals, m. p. above 280°. 7-m-*Xylidino*-10-m-*xylylsafranol*, $C_{28}H_{25}O_2N_3$, m. p. above 300°, microscopic, red plates, and 7-p-*amino-anilino*-10-p-*aminophenylsafranol*,

$$NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2(OH)<\overset{N}{\underset{N(C_6H_4\cdot NH_2)}{}}>C_6H_3{:}O,$$

are described; the latter is the only one of these safranols of which the *hydrochloride*, $C_{24}H_{19}O_2N_5,3HCl$, has been isolated. (In the formulæ of these safranols, the hydroxylic hydrogen atom may be attached to either of the oxygen atoms.)

The oxidation by sodium hypochlorite of a mixture of *p*-aminophenol and *m*-cresol in alkaline solution at −10° yields the *sodium* salt, olive-green needles, of *methylindophenol*, m. p. 124°, metallic green crystals. This substance may have the formula

$$OH\cdot C_6H_3Me\cdot N{:}C_6N_4{:}O$$

or $O{:}C_6H_3Me{:}N\cdot C_6H_4\cdot OH$. However, it is not tautomeric, and receives the former constitution because it yields toluquinol, m. p. 124°, by decomposition by dilute hydrochloric acid. By reduction with alkaline sodium hyposulphite, it yields pp′-*dihydroxyphenyl*-o-*tolylamine*, the *dibenzoyl* derivative of which has m. p. 132—133°. This methylindophenol yields dianilino- and dianilo-derivatives and a safranol by methods similar to those described above; *di*-p-*toluidino-methylindophenol*, $C_{27}H_{25}O_2N_3$, m. p. 203°, brownish-black needles, *di*-p-*toluidomethylindophenol*, $C_{27}H_{23}O_2N_3$, m. p. 251°, orange needles, and 7-p-*toluidino*-10-p-*tolyl*-1-*methylsafronal*, $C_{27}H_{23}O_2N_3$, m. p. above 300°, are described.

The alternative constitution, $O{:}C_6H_3Me{:}N\cdot C_6H_4\cdot OH$, is ascribed to

the *methylindophenol*, m. p. 178—179°, reddish-brown needles, which is obtained by the oxidation of phenol and 6-amino-*m*-cresol by cold alkaline sodium hypochlorite.

By similar processes of oxidation, *p*-aminophenol and *o*-cresol yield a *methylindophenol*, which forms an *anilino*-derivative, $C_{19}H_{16}O_2N_2$, m. p. 223—224°, crystalline powder, and phenol and 5-amino-*o*-cresol yield an isomeric *methylindophenol*, which forms a *dianilino*-derivative, $C_{25}H_{21}O_2N_3$, m. p. 167—168°, blackish-brown leaflets.

Phenol-blue is most conveniently prepared by oxidising a mixture of phenol and *as*-dimethyl-*p*-phenylenediamine by alkaline sodium hypochlorite at 0° (Gnehm, Abstr., 1904, i, 451). It has m. p. 167° (not 160°), is decomposed by dilute hydrochloric acid, yielding quinol at the ordinary temperature and *p*-benzoquinone at higher temperatures, and reacts with alcoholic aniline, best at 50—60°, to form *dianilinophenol-blue*, $C_{26}H_{24}ON_4$, m. p. 226°, brown needles. α-Naphthol-blue is prepared in a similar manner.

Interaction with primary aromatic amines at the ordinary temperature is characteristic of indophenols; indamines do not exhibit such behaviour.

The oxidation of *p*-phenylenediamine and phenol in aqueous sodium hydrogen phosphate and sodium hydrogen carbonate by lead peroxide at 7° (D.R.-P. 179294) yields 4-*hydroxyindamine*,

$$NH\!:\!C_6H_4\!:\!N\cdot C_6H_4\cdot OH,$$

m. p. 105—106°, blue needles; in a similar manner, *p*-phenylenediamine and *m*-cresol yield 4-*hydroxy*-2-*methylindamine*,

$$NH\!:\!C_6N_4\!:\!N\cdot C_6H_3Me\cdot OH,$$

m. p. 143—144°, blue needles. These two dyes receive the constitutions depicted, because they are soluble in alkalis and yield quinol by decomposition with dilute hydrochloric acid. 4′-*Amino*-3-*methylindophenol* (?), m. p. 154—155°, obtained from *p*-phenylenediamine and *o*-cresol, receives the constitution $NH_2\cdot C_6N_4\cdot N\!:\!C_6H_3Me\!:\!O$, because of its insolubility in alkalis.

By reduction with zinc and acetic acid or with alkaline sodium hyposulphite, the three dyes are respectively converted into colourless leuco-compounds, which are re-oxidised by atmospheric oxygen.

C. S.

Constitution of the Compound Derived from Benzoylchlorocarbamide and Alkali. OTTO DIELS and HARUKICHI OKADA (*Ber.*, 1912, **45**, 2437—2441).—As shown by Diels and Wagner (this vol., i, 511), benzoylchlorocarbamide when acted on by dilute alkali loses a molecule of hydrogen chloride, and is converted into a substance to which the structure $\begin{matrix} COPh\cdot N \\ HN \end{matrix}\!\!>\!CO$ is assigned. The compound has now been further studied.

It is converted by aqueous hydrogen chloride or by hydrogen bromide in acetic acid into benzoic acid, and the corresponding salt of hydrazine. When heated with aniline, diphenylcarbamide, and benzhydrazide are obtained.

On heating with hydrazine hydrate, the 3-membered ring is broken, *benzoylcarbohydrazide*, $COPh\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2$, being formed,

which on further heating breaks down into benzoic acid and carbohydrazide.

Mild reducing agents eliminate carbon dioxide and reduce it to benzylhydrazine.

Benzoylcarbohydrazide crystallises in colourless plates with a fatty lustre, m. p. 186°, which reduce Fehling's solution. E. F. A.

Action of Hydrazine on Dicyanodiamide. KARL A. HOFMANN and OSKAR EHRHARD (*Ber.*, 1912, **45**, 2731—2740).—The authors have re-examined the action of hydrazine on dicyanodiamide, and assign to melamazine the formula $C_6N_{12}H_6,H_2O$ in place of $C_6N_{12}H_8,H_2O$, that previously adopted (Abstr., 1911, i, 843). They now adopt the name trisdeamidoguanazole, or, more shortly, pyroguanazole.

If a mixture of dicyanodiamide and hydrazine hydrate is exposed to air at the ordinary temperature, an intensely red coloration appears. Probably the $-C{\equiv}N$ group of the dicyanodiamide reacts with hydrazine hydrate to form a readily oxidisable hydrotetrazine. This is the more probable, since benzonitrile in alcoholic solution under the action of hydrazine hydrate and air deposits diphenyltetrazine (compare Pinner, Abstr., 1898, i, 94). Acetonitrile, however, under similar conditions, yields methylhydrazincarbimine,

$$NH{:}CMe{\cdot}NH{\cdot}NH{\cdot}CMe{:}NH.$$

When dicyanodiamide and hydrazine hydrate are heated on the water-bath, a good yield of guanazole is obtained (compare Pellizzari, Abstr., 1892, i, 356; 1894, i, 517), which, when heated at 275° during thirty minutes, is transformed into pyroguanazole, one molecule of ammonia being evolved from each molecule of guanazole. *Pyroguanazole hydrochloride* separates from solution in concentrated hydrochloric acid $+2HCl$; from dilute hydrochloric acid, on the other hand, $+HCl$. The *platinichloride*, $(C_6N_{12}H_6,H_2O)_4H_2PtCl_6$, was analysed. A *penta-acetyl* derivative was obtained by the prolonged action of acetic anhydride or pyroguanazole at 125°.

Pyroguanazole, when oxidised by hot acid potassium permanganate, evolves six atoms of nitrogen from each molecule of substance. In alkaline solution, however, only four atoms of nitrogen are eliminated, cyanuric acid together with a yellow *product*, $C_4H_4O_2N_6$, being formed. The latter evolves ammonia when heated with potassium hydroxide, and yields a *silver* salt, $C_4H_2O_2N_6Ag_2$. It probably has the constitution $HN{<}{\substack{CO{-\!\!-}NH\\C({:}NH){\cdot}N}}{>}C{\substack{\nearrow N\\ \searrow N}}{>}C{\cdot}OH.$

Towards acids, pyroguanazole exhibits extraordinary stability. Concentrated sulphuric acid does not decompose it at 170°, but, after twenty-four hours' heating with hydrochloric acid (20%), it is resolved into carbon dioxide, ammonium chloride, and hydrazine chloride. Prolonged treatment with Caro's acid yields a yellow *product*, which, on treatment with ammonia, gives a yellow *powder* of the approximate constitution $C_6H_3O_3N_9,2NH_3$, and, when acted on by ammoniacal silver nitrate, a brown *silver* salt, $C_6O_3N_9Ag_3,3NH_3$. Thus, the hydrazine portion of the molecule appears to be oxidised by Caro's acid.

In the absence of oxygen, pyroguanazole is soluble in alkali with the formation of a colourless solution, which, however, readily absorbs

oxygen with simultaneous elimination of nitrogen and formation of an intensely bluish-violet solution, from which a *thallium* salt,

$$C_6N_{11}H_3Tl_2O,$$

may be obtained. At a higher temperature, an additional quantity of nitrogen is evolved, and the previously-described thallium salt (Abstr., 1911, i, 843) is obtained. At the same time, the number of acetyl groups which can be introduced into the molecule by means of acetic anhydride sinks from five to about two. The composition of the bluish-violet substance remains somewhat uncertain, since it is readily acted on by air. If the alkaline solution is evaporated in the presence of air, it becomes deep brown in colour, and yields a *silver* salt, $C_4H_3ON_7Ag_2,NH_3$, when treated with ammoniacal silver nitrate solution. The same oxidation product is more readily obtained by oxidation of an alkaline solution of pyroguanazole by hydrogen peroxide, and then yields an *ammonium* salt, $(C_4N_7OH_5)_2NH_3$, which when boiled with acid potassium permanganate, evolves one molecule of nitrogen from each molecule, $C_4N_7OH_5$, and probably has the constitution represented by the formula $\begin{array}{l} C(NH)\cdot NH\cdot C:N \\ NH—C(NH)N\cdot N \end{array} \!\!> C\cdot OH$.

H. W.

p-Dimethylaminobenzenediazonium Chloride. ROBERT STOLLÉ (*Ber.*, 1912, **45**, 2680—2685).—In addition to dibenzoylhydrazide and tetramethyldi-*p*-aminodiphenylmethane (compare this vol., i, 225), the interaction of azodibenzoyl and dimethylaniline yields a small amount of an additive compound which is considered to be *dibenzoyl*-p-*dimethylaminophenylhydrazide*, $NMe_2\cdot C_6H_4\cdot NBz\cdot NHBz$. This has m. p. 199°, and on hydrolysis yields *p*-aminodimethylaniline and benzoic acid. With the object of confirming the above formula by the direct synthesis of the dibenzoyl derivative from *p*-dimethylaminophenylhydrazine, the authors have attempted to prepare the latter compound (1) by the reduction of *p*-dimethylaminobenzenediazonium chloride with stannous chloride, and (2) by the successive action of sodium hydrogen sulphite and hydrochloric acid on sodium *p*-dimethylaminobenzeneazosulphonate in aqueous solution. It was found, however, that the reduction of the diazonium chloride gave rise to *p*-aminodimethylaniline and ammonia, whilst in the second case the action of hydrochloric acid on the intermediately formed *p*-dimethylaminophenylhydrazinesulphonic acid resulted in the removal of both the sulphonic acid and *p*-dimethylaminophenyl groups with the formation of hydrazine.

p-Dimethylaminobenzenediazonium chloride is obtained in pale yellow crystals exploding at 130° by the action of amyl nitrite on *p*-aminodimethylaniline in alcoholic solution (compare Hantzsch, Abstr., 1902, i, 325). It combines with stannous chloride in the presence of hydrochloric acid, yielding a crystalline *stannichloride*, $C_8H_{10}N_3Cl,SnCl_2,HCl$, and with mercuric chloride in alcoholic solution to form the *compound*, $C_8H_{10}N_3Cl,HgCl_2$, which crystallises in needles, m. p. 150° (decomp.).

p-*Dimethylaminobenzenediazonium sulphate*, prepared in a similar manner, crystallises in pale green leaflets, m. p. 158° (decomp.).

p-*Dimethylaminobenzeneazosulphonic acid*, $C_8H_{11}O_3N_3S$, obtained in the form of its *sodium* salt (orange-yellow needles) by the interaction of *p*-dimethylaminobenzenediazonium chloride and sodium hydrogen sulphite in aqueous solution, crystallises in violet-red prisms, m. p. 144°; the *potassium* salt, brick-red needles, and *silver* salt, violet-red needles, are also described. Its alcoholic solution is reduced by stannous chloride and hydrogen chloride in ethereal solution to p-*dimethylaminophenylhydrazinesulphonic acid*, which forms pale green leaflets, m. p. 189°, and is hydrolysed by water or hydrochloric acid to *p*-aminodimethylaniline. The *dibenzoyl* derivative of the last-mentioned compound crystallises in prisms, m. p. 240°. F. B.

***o*-Aminoazobenzene.** FELIX H. WITT (*Ber.*, 1912, **45**, 2380—2384).—*o*-Nitroaniline is most conveniently benzoylated by treatment with benzoyl chloride and diethylaniline on the water-bath; the yield is 96–98% of the theoretical.

Benzoyl-*p*-phenylenediamine and nitrosobenzene condense in a cold mixture of glacial acetic acid and alcohol (10 : 4) to form o-*benzoylaminoazobenzene*, $NHBz \cdot C_6H_4 \cdot N_2Ph$, m. p. 122°, reddish-yellow needles, the hydrolysis of which by boiling alcoholic sodium ethoxide yields o-*aminoazobenzene*, m. p. 59°, garnet-red, monoclinic prisms. The orange-yellow *sulphate*, $C_{12}H_{13}N_3,H_2SO_4$, *hydrochloride*, yellow needles, and *acetyl* derivative, m. p. 126°, reddish-yellow needles, are described. The substance yields aniline and *o*-phenylenediamine by fissive reduction, and phenylaziminobenzene by oxidation by chromic and acetic acids. C. S.

The Change in Hydrogen Ion Concentration during Heat Coagulation of Proteins. G. QUAGLIARIELLO (*Biochem. Zeitsch*, 1912, **44**, 157—161).—A solution of coagulated albumin is always electrically negative towards the corresponding solution of uncoagulated protein, owing to diminution of the hydrogen ion concentration. This change in concentration can also be detected when the coagulation has only proceeded so far that there is no macroscopic alteration in the liquid. It is then only small, but becomes larger with progressive coagulative change, reaching its maximum with the agglutination of the protein. The magnitude of the change also depends on the acid used in the solution, being less for acetic than for hydrochloric and nitric acids. The concentration necessary for flocculation is independent of the nature of the acid. In normal sodium chloride or nitrate solutions, the protein separates in a flocculent form at room temperature on addition of acids. This happened in the cases of hydrochloric and nitric acids at a concentration of $0{\cdot}05N$, and in acetic acid at the concentration $0{\cdot}5N$. Subsequent warming causes no further change in the hydrogen ion concentration. The changes in this concentration on heat coagulation cannot therefore be due to elimination of carbon dioxide. In solutions in which the protein separated on heat coagulation, the hydrogen ion concentration diminished by about 50% of the original value; when no flocculation occurred, the diminution was only 5—7%. S. B. S.

Heat Coagulation of Proteins. IV. The Conditions Controlling the Agglutination of Proteins Already Acted Upon by Hot Water. HARRIETTE CHICK and CHARLES J. MARTIN (*J. Physiol.*, 1912, **45**, 261—295. Compare this vol., i, 734).—Previous papers have dealt more specially with the first phase in heat coagulation, namely, denaturation of the protein. The present research relates to the second phase, agglutination which follows it. Dispersion of denaturated protein by acid and alkali is due to the electric charge given to the particles. If this is neutralised and the proteins become isoelectric with the solution, agglutination occurs. The optimum acidity for precipitation in the absence of electrolytes is equal to a concentration of hydrogen ions of about 3×10^6 *N*. Agglutination is influenced by neutral salts by (*a*) alterations in the concentration of hydrogen ions, or by (*b*) neutralisation or increase of the electric charge carried by the protein particles. Dispersion by salts is due to the adsorption of ions by the denaturated particles. For every solution containing denaturated protein there is a critical temperature depending on the reaction and on the concentration of protein and electrolytes, below which agglutination does not take place. The supposed conversion of albumin into globulin by heating the former in an alkaline solution (Starke, Moll) is simply explained by differences in the state of aggregation. The substance supposed to be globulin is merely heat-denaturated protein in a loose state of aggregation. W. D. H.

Hydrogen Peroxide as a Hydrolysing Agent. NADINE SIEBER (*Zeitsch. physiol. Chem.*, 1912, **81**, 185—199).—Experiments in which various proteins (keratin, casein, hæmoglobin, etc.), and also tubercle bacilli were heated under pressure with hydrogen peroxide, show that cleavage takes place, so supporting the view that this reagent is not only an oxidising, but also a hydrolysing, agent. W. D. H.

The Xanthoproteic Reaction. KATSUJI INOUYE (*Zeitsch. physiol. Chem.*, 1912, **81**, 80—85).—The exact meaning of the protein colour reactions is still far from clear, although it is certain that the majority are reactions of certain cleavage products of the protein molecule. The xanthoproteic reaction is given by a number of protein "Bausteine." In the present research, silk fibroin was used, and from the coloured product due to the action of nitric acid, a mononitrotyrosine was separated. Whether a similar compound with phenylalanine occurs is not yet ascertained. W. H. D.

The Polarimetric Estimation of the Glucosamine Content of Ovomucoid and Pseudomucin. CARL NEUBERG and OMER SCHEWKET (*Biochem. Zeitsch.*, 1912, **44**, 491—494).—The proteins were hydrolysed with hydrochloric acid, and the amino-acids, etc., were precipitated according to the method of Neuberg and Ishida, first by mercuric acetate and then by phosphotungstic acid. The glucosamine was then estimated in the colourless filtrate polarimetrically. By this method ovomucoid was found to contain 24%, and pseudomucin 36·6%, of glucosamine. S. B. S.

Action of Hydroxylamine on the Blood Colouring Matter. Methæmoglobin. EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1912, **80**, 412—429).—By the action of hydroxylamine, oxyhæmoglobin is converted quantitatively into methæmoglobin having the spectrophotometric quotient 1·186°. Nitrogen is liberated at the same time, produced from hydroxylamine by the oxidising action of the oxyhæmoglobin. This is in agreement with Küster's suggestion that methæmoglobin contains less oxygen than oxyhæmoglobin.

The absorption ratio for methæmoglobin in the region 556·1—564·6 $\mu\mu$ is $2 \cdot 103 \times 10^{-3}$. Hydroxylamine acts as an oxidising agent towards reduced hæmoglobin. E. F. A.

Preparation and Recrystallisation of Hæmin. ANT. HAMSIK (*Zeitsch. physiol. Chem.*, 1912, **80**, 35—44).—Hæmatin has been split off from oxyhæmoglobin by continued boiling with sufficiently concentrated aqueous potassium hydroxide, and the preparation of hæmin from this material studied in acetone, glacial acetic acid, and ethyl-alcoholic solutions. Characteristic hæmin crystals having the composition $C_{34}H_{32}O_4N_4ClFe$ were obtained in each case. Unsatisfactory results were obtained in attempting to prepare hæmin from the hæmatin prepared originally from hæmin. E. F. A.

Molecular Size of Hæmin and Hæmoglobin. OSCAR PILOTY and H. FINK (*Ber.*, 1912, **45**, 2495—2498).—The molecular weight of hæmatoporphyrin has been shown by Piloty and Dorn (this vol., i, 519) to be about 1200. No simple derivatives of hæmin are available to test whether a doubling of the molecule does not take place in the formation of hæmatoporphyrin from hæmin. Mesoporphyrin obtained by the action of hydrogen iodide has a molecular weight not above 600, corresponding with about half that of hæmatoporphyrin. During its formation losses may arise due to incomplete action on hæmatoporphyrin or due to the formation of more simple substances, such as hæmopyrrole. The maximum yield obtained is 39·2%, which makes it probable that it is derived from only one-half of the hæmin molecule. Accordingly, the molecular weight of hæmin is about 1303, and that of hæmoglobin about 30,000. The coloured portion of hæmoglobin consists of eight and not of four pyrrole nuclei, as previously supposed. E. F. A.

Oxidation of Dimethylhæmin. WILLIAM KÜSTER and ALFRED GREINER (*Ber.*, 1912, **45**, 2503—2504. Compare this vol., i, 670).—On oxidation of dimethylhæmin with chromium trioxide in acetic acid, some 42% of the theoretical yield of methylhæmatinic acid is obtained. This on hydrolysis yields pure hæmatinic acid. This behaviour indicates that the hæmin molecule contains two carbonyl groups. E. F. A.

Pigment of the Blood. IV. Hæmopyrrole. OSCAR PILOTY and JOSEF STOCK (*Annalen*, 1912, **392**, 215—244).—"Hæmopyrrole," obtained from the blood or from chlorophyll derivatives, is a mixture (Piloty and Quitmann, Abstr., 1910, i, 133). In addition to the

hæmopyrrole, *iso*hæmopyrrole, and phyllopyrrole isolated by Willstätter and Asahina (this vol., i, 41), the authors have succeeded in obtaining new constituents. Since the name hæmopyrrole is now used in the literature to denote four different substances, some system of nomenclature is very necessary. The authors retain the name hæmopyrrole to denote the whole mixture, the constituents of which are then denoted by hæmopyrrole-*a*, -*b*, -*c*, etc., in the order of their b. p.'s.

A large quantity, 320 grams, of crude hæmopyrrole, obtained from 1400 grams of hæmin by Nencki and Zaleski's method, has been submitted in succession to fractional distillation, fractional precipitation with ethereal picric acid, and fractional crystallisation of the picrates. The following substances of definite constitution have thereby been isolated: (1) Hæmopyrrole-*a*, $C_7H_{11}N$, b. p. 81°/18 mm., which does not form a crystalline picrate, yields methylethylmaleimide by oxidation with chromic acid, and is therefore 3-methyl-4-ethylpyrrole. (2) Hæmopyrrole-*b* (2:3-dimethyl-4-ethylpyrrole), m. p. about 16°, b. p. 87—88·5°/12·5 mm. (picrate, m. p. 122·5°), which is Willstätter and Asahina's *iso*hæmopyrrole (*loc. cit.*). (3) Hæmopyrrole-*c* (3:5-dimethyl-4-ethylpyrrole), b. p. 84—85°/13 mm. (picrate, m. p. 137·5°), which is identical with Knorr and Hess's synthetic compound (Abstr., 1911, i, 1019). (4) Hæmopyrrole-*d* (2:3:5-trimethyl-4-ethylpyrrole) is identical with Willstätter and Asahina's phyllopyrrole (*loc. cit.*) synthesised by Fischer and Bartholomäus (this vol., i, 297). (5) *Bishaemopyrrole*-e (*bis*-2:3-*dimethyl*-1-*ethylpyrrole*, $CMe{<}\begin{matrix}CMe\cdot CH\cdot CH\cdot CMe\\ NEt\cdot CH\cdot CH{-}NEt\end{matrix}{>}CMe$ [?]), an oil, which forms a *picrate*, $C_{22}H_{29}O_7N_5$, m. p. 148°, small, red needles. Willstätter and Asahina's hæmopyrrole (*loc. cit.*) is shown to be a mixture of hæmopyrroles-*b* and -*c*.

Hæmopyrroles-*a*, -*b*, -*c* each yield methylethylmaleimide by oxidation. At least two of them should yield the same oxime. The fact that they form different oximes, m. p. 197—198°, 221·5°, and 215° respectively, apparently renders necessary the introduction of stereochemical constitutions. C. S.

Phonopyrrolecarboxylic Acid and its Companions. OSCAR PILOTY and E. DORMANN (*Ber.*, 1912, **45**, 2592—2595).—It has recently been shown (this vol., i, 519) that the reduction of hæmin by hydriodic acid and phosphonium iodide gives rise to phono- and xantho-pyrrolecarboxylic acids, which very closely resemble the *iso*phonopyrrolecarboxylic acid obtained by Piloty and Thannhauser (this vol., i, 736) by the action of hydriodic acid on bilirubin.

In view of the great similarity of the acids and the difficulty of separating and characterising them, the authors have subjected the phonopyrrolecarboxylic acid, obtained from hæmin, to fractional precipitation with picric acid in order to determine whether it is accompanied by *iso*phonopyrrolecarboxylic acid. It is found that the crude phonopyrrolecarboxylic acid yields two picrates, m. p. 138·5 and 146°, of which the less fusible one is apparently identical with the picrate of *iso*phonopyrrolecarboxylic acid, and yields an acid m. p. 118—122°. On treatment with nitrous acid, this gives rise to two oximes, one of

which is identical with the oxime previously obtained from phonopyrrolecarboxylic acid, whilst the other sinters at 202°, becomes brown at 212°, and has m. p. 227° (decomp.) It is also found that the picrate of m. p. 138·5° is not a single chemical individual, but is derived from a mixture of acids. From these results the conclusion is drawn that phonopyrrolecarboxylic acid is accompanied by several closely related acids. When boiled with methyl alcohol the yellow picrate of the acid mixture is converted into a brown picrate, $C_{15}H_{16}O_9N_4$, crystallising in prismatic needles, m. p. 122°. On decomposition with aqueous potassium hydroxide, the brown picrate yields phonopyrrolecarboxylic acid (yellow picrate, m. p. 158—159°), together with an *acid* which crystallises in long, flat, radiating needles, m. p. 58°, and forms a brown *picrate*, $C_{16}H_{18}O_9N_4$ (?), m. p. 120°. F. B.

Hæmatopyrrolidinic Acid. OSCAR PILOTY and P. HIRSCH (*Ber.*, 1912, **45**, 2595—2600).—From the amorphous character of the acid itself and also of its picrate, it would appear that hæmatopyrrolidinic acid is not a single chemical individual, but consists of a mixture of substances of very similar structure and composition. It is suggested that the picrate, which has a constant composition, is a double picrate of two closely allied substances, of which one has the constitution :

$$\begin{array}{l}\mathrm{CMe{-\!\!-\!\!-}CH\cdot CH(CH_2\cdot CO_2H)\cdot CH\cdot NH\cdot CMe} \\ \;\| \qquad\quad\; | \qquad\qquad\qquad\qquad\quad | \qquad\qquad\; \| \\ \mathrm{CMe\cdot NH\cdot CH{-\!\!-\!\!-}CHMe{-\!\!-\!\!-}CH{-\!\!-\!\!-}CMe'}\end{array}$$

whilst the other consists of a compound of similar structure, but in a lower state of reduction, or is derived from a hæmopyrrole, isomeric with that which forms the basis of the above formula. This suggestion receives support from the results obtained in a re-examination of the pyrrole mixture obtained by Piloty and Merzbacher (Abstr., 1909, i, 857) by fusing zinc hæmatopyrrolidinate with potassium hydroxide.

The following substances were isolated from the pyrrole mixture by fractional distillation and fractional precipitation with picric acid: (1) 2:3-Dimethylpyrrole (this vol., i, 736). (2) A hæmopyrrole, b. p. 84—86°/12 mm., which forms a picrate, m. p. 109—112°, and on treatment with nitrous acid yields an oxime (decomp. 201°). (3) A pyrroline, which forms a picrate, $C_{14}H_{18}O_7N_4$, m. p. 144°, and is probably identical with the pyrroline isolated in the form of its picrate by Piloty and Quitmann (Abstr., 1910, i, 133) from the product obtained by the action of hydriodic acid on hæmatoporphyrin. (4) An oil, b. p. 73—76°/10·5 mm., which has the composition $C_7H_{11}N$, and consists of a mixture of pyrroles. On treatment with nitrous acid it does not yield an oxime, but is oxidised to citraconimide and a mixture of maleimides. The isolation of the pyrroline furnishes strong evidence in favour of the above formula. F. B.

Dehydrobilic Acid, a Coloured Oxidation Product of Bilic Acid. OSCAR PILOTY and J. S. THANNHAUSER (*Ber.*, 1912, **45**, 2393—2395).—By oxidation with aqueous potassium permanganate below 7°, sodium bilate (this vol., i, 736) yields, after acidification of the filtered solution, *dehydrobilic acid*, $C_{17}H_{22}O_3N_2$, decomp. above 260°, citron-yellow prisms, which does not respond to the pine-shaving test or react with *p*-dimethylaminobenzaldehyde, and forms a *sodium*

salt, yellow needles. Accepting the authors' formula of bilic acid (*loc. cit.*), the colour of dehydrobilic acid may be accounted for by the presence of a system of conjugated double linkings. C. S.

Behaviour of the True Nucleic Acids to Dyes. I. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1912, 80, 73—78).—When sodium nucleate and the chloride of malachite-green are brought together, a double interaction takes place with the formation of sodium chloride and the nucleate of malachite-green. This compound is a black, porous mass with a red surface reflex; the absence of chlorine from it is against the assumption that it is an adsorption compound. E. F. A.

Guanine Hexoside Obtained on Hydrolysis of Thymus-nucleic Acid. PHŒBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 377—380).—Previous investigations by the authors have shown that plant nucleic acid yields various pentosides. Direct proof that the purine bases have the same glycosidic union in thymus-nucleic acid is, however, wanting. Repeated attempts to obtain the nucleosides from thymus-nucleic acid by the same methods failed; but by the employment of an enzyme, the source and nature of which are not given, a guanine hexoside, $C_{11}N_{15}O_6N_5$, was separated. It is semi-crystalline, soluble in hot alcohol, does not reduce Fehling's solution, and only gave the orcinol test in the presence of copper. From the products of hydrolysis, an osazone melting at 198° and guauine sulphate were obtained. W. D. H.

Structure of Thymus-nucleic Acid. PHŒBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 411—420).—The separation of yeast-nucleic acid into its constituent nucleotides is due to the stability of the carbohydrate ribose which they contain. The instability of the hexose in thymus-nucleic acid leads to difficulties in decomposing this by the same methods, a part being at once cleaved into lævulinic acid. As the nature of the hexose is still uncertain, the structural formulæ given in the paper are regarded as provisional only. The crystalline brucine and barium salt of a dinucleotide containing thymine and cytosine was examined, and the conclusion drawn that each phosphoric acid group contains a secondary and a tertiary hydroxyl, and that the linking between the nucleotides occurs between the sugar groups.
W. D. H.

Guanylic Acid. PHŒBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 421—426).—Although Bang does not accept the view that guanylic acid is a simple mono-nucleotide, recently-ascertained facts support the idea. It is now possible to obtain the substance in the form of a pure crystalline brucine salt, and analysis of this confirms the authors' hypothesis. There is, however, more basis for the assumption that the structure of guanylic acid is not identical with that of inosinic acid. Both guanylic and yeast-nucleic acids permit the detaching of phosphoric acid quite easily, whereas in inosinic and thymus-nucleic acids the same is accomplished with difficulty. This is probably due to a difference in the position of the

phosphoric acid on the sugar, but definite evidence of the position has not yet been forthcoming. W. D. H.

Action of Saliva, Tissue Fluids, Bacteria, and Bacterial Extracts on Polypeptides. J. W. TAYLOR and I. WALKER HALL (*J. Path. Bact.*, 1912, **17**, 121—123).—Saliva, blood, exudations, and transudations from the blood, certain bacteria, and bacterial extracts were found capable of splitting glycyl-*l*-tryptophan. The liberation of tryptophan, and the ease with which this substance can be detected, render this test an easy one for the demonstration of peptolytic enzymes. W. D. H.

The Thermostability of Trypsin and Pepsin. KOHSHI OHTA (*Biochem. Zeitsch.*, 1912, **44**, 472—480).—It has been claimed by E. W. Schmidt that trypsin still retains its activity when heated to 100° in water in the presence of various colloids, such as peptone, gelatin, or agar-agar. The author has repeated these experiments, using various methods to detect proteoclastic activity, and has failed to confirm Schmidt's observations. He has also tried the same experiments with pepsin, and has failed to obtain an active preparation after heating various ferment solutions in water at 100° in the presence of colloids. S. B. S.

Diastase. II. The Preparation of Pure Diastase and its Properties. ERNST PŘIBRAM (*Biochem. Zeitsch.*, 1912, **44**, 293—302. Compare Fränkel and Hamburg, Abstr., 1906, i, 917).—In order to prepare diastase from malt extract, it is not necessary to use pure yeast cultures to destroy the sugars if the ferment mixture is not allowed to get too acid by the formation of lactic acid. The preparation was made therefore from Pilzen malt, the mash being prevented from becoming acid by the addition of calcium carbonate. The sugar-free filtrate of the fermentation mixture is then evaporated to a syrup, and filtered from the calcium lactate which separates. Although the diastase does not dialyse through parchment, it can be filtered through gelatin filters under pressure, and the author describes (with figures) the apparatus employed for this purpose. Most experiments were carried out with the dialysed preparation. The dried preparation purified in this way contains 7·7% nitrogen and 1·5% ash. Fifteen % of the nitrogenous matter separates as a coagulum on heating, which gives a strong reaction with Millon's reagent, but a very weak biuret reaction. The filtrate on hydrolysis with sulphuric acid yields a reducing substance, which does not form an osazone, but forms a barium salt, and is probably a polycarbohydrate acid ; it exists in the ferment in combination with a somewhat simple polypeptide. The purified diastase is inactive, but is activated by the addition of traces of lactic acid. S. B. S.

The Influence of Antiseptics on the Action of Maltase. W. KOPACZEWSKI (*Biochem. Zeitsch.*, 1912, **44**, 349—352).—The best antiseptics for employment in investigating the action of maltase on sugars are toluene and chloroform. Mustard oil is inconvenient, as its

reducing action interferes with the estimation of sugars. If sodium fluoride is used, the optimal concentration is 0·4—0·5%. In this concentration the action of the ferment is accelerated. Formaldehyde has an inhibitory action, which can be detected in a concentration of 0·1%. The hydrogen ions exert a deleterious action even in relatively low concentrations. S. B. S.

The Reversibility of Ferment Actions. Influence of the Dilution of Ethyl Alcohol on the Synthesising Action of Emulsin in this Medium. EMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, **155**, 319—322. Compare this vol., i, 592, 593, 672; Bertrand and Compton, this vol., i, 592).—Numerous attempts have been made, without success, to synthesise disaccharides by means of enzymes from the products of their hydrolysis by the same enzymes (compare Croft Hill, Trans., 1898, **73**, 634; 1903, **80**, 578). The authors have set up experiments with mixtures of β-ethyl glucoside and alcohol (85%), and dextrose and alcohol (85%), in separate flasks, the amounts of glucoside and dextrose used being equivalent. To each mixture was added the same amount of emulsin, and they were left at the ordinary temperature with occasional shaking for sixteen to twenty-one days, when the two liquids were found to have exactly the same rotation. By varying the strength of the alcohol, the actual final rotation, whilst being the same for the two mixtures, was found to vary with the strength of the alcohol used. The more dilute the alcohol, the greater is the hydrolysis and the less the synthesis, and vice versa. W. G.

Action of Enzymes on Hexose Phosphate. VICTOR J. HARDING (*Proc. Roy. Soc.*, 1912, *B*, **85**, 418—422).—Hexose phosphate is slowly hydrolysed by Ricinus lipase and by emulsin from almonds, whilst the autolysed pancreas of the ox is almost without action. An aqueous extract of zymin hydrolyses hexose sulphate slowly. Autolysed yeast-juice possesses a very marked hydrolytic action, and the enzyme effecting this hydrolysis may be precipitated from the juice with a mixture of alcohol and ether. W. J. Y.

New Properties of Peroxydases and their Behaviour in the Absence of Peroxides. JULES WOLFF (*Compt. rend.*, 1912, **155**, 618—620).—Peroxydase, from young barley shoots, produces a marked catalytic effect on the rate of oxidation of orcinol, in the presence of alkali hydroxides or carbonates, by atmospheric oxygen without any peroxides being present. The same relative increase in oxidation is noticed if the alkalis are replaced by sodium phosphate. W. G.

1:4-Dichloroarsinobenzoyl Chloride. Esters of Benzarsinious and Benzarsinic Acids. ERNEST FOURNEAU and OCHSLIN (*Bull. Soc. chim.*, 1912, [iv], **11**, 909—914).—The preparation of 1:4-dichloroarsinobenzoyl chloride and of a number of its derivatives are described.

Benzarsinic acid, $AsO(OH)_2·C_6H_4·CO_2H$ (p-carboxyphenylarsinic

acid, Abstr., 1908, i, 591), on treatment with phosphorus trichloride in chloroform yields benzarsinious dichloride (*p*-carboxyphenylarsinious chloride), $AsCl_2\cdot C_6H_4\cdot CO_2H$, already obtained by La Coste (Abstr., 1881, 903), and this by the further action of phosphorus pentachloride is converted into *dichloroarsinobenzoyl chloride*, $AsCl_2\cdot C_6H_4\cdot COCl$, b. p. 189—190°/19 mm., a mobile liquid, which fumes in moist air, is soluble in chloroform or benzene, and on keeping passes into a crystalline mass. It reacts like an acid chloride with hydroxy-compounds. When it is dissolved in alcohol and the mixture treated with water, *ethyl arsinobenzoate oxide*, $AsO\cdot C_6H_4\cdot CO_2Et$, m. p. 277°, is precipitated as an amorphous powder, from which sodium hydroxide solution liberates the corresponding *acid*, $AsO\cdot C_6H_4\cdot CO_2H$, brilliant flat needles, which does not melt up to 280°.

On oxidation with hydrogen peroxide in alkalis, the oxide is converted into *ethyl benzarsinate* (p-*carbethoxyphenylarsinic acid*), $AsO(OH)_2\cdot C_6H_4\cdot CO_2Et$, m. p. 260° (decomp.), crystallising in small brilliant spangles. The *quinine* salt, similarly prepared, in two stages, forms small, brilliant cubes, m. p. 200° (approx.), is sparingly soluble in organic solvents, but is readily dissolved by acids or alkalis. A sodium carbonate solution of the salt on treatment with sodium hyposulphite yields *benzarsenoquinine*, $As_2(C_6H_4\cdot CO_2,C_{20}H_{23}O_2N_2)_2$, as a bright yellow powder.

Stovaine, $C_2H_5\cdot CMe(OBz)\cdot CH_2\cdot NMe_2,HCl$, has a special affinity for nerve substance, and its arsenical analogue has been prepared by treating dimethylaminodimethylethylcarbinol with dichloroarsinobenzoyl chloride. The resulting *dichloroarsinobenzoate hydrochloride*, $C_{14}H_{20}O_2N,HCl$, m. p. 194°, crystallises in small, colourless needles from alcohol, but has not been obtained free from the corresponding *oxide*, $C_2H_5\cdot CMe(O\cdot CO\cdot C_6H_4\cdot AsO)\cdot CH_2\cdot NMe_2$, which can be prepared by treating the compound just described with sodium carbonate solution in presence of ether to remove it as formed; it is a viscous oil, as is also its *hydrochloride*; the latter produces on the tongue an intense and persistent tingling. On reduction with sodium hyposulphite, the oxide yields *arsenostovaine*, $C_{28}H_{40}O_4N_2As_2$, as a golden-yellow powder, soluble in acids.

Guaiacyl arsinobenzoate oxide, m. p. 191°, obtained by the action of dichloroarsinobenzoyl chloride on guaiacol dissolved in benzene in presence of pyridine, crystallises in tufts of colourless needles, and on oxidation with hydrogen peroxide in acetone yields *guaiacyl benzarsinate*, which crystallises in brilliant, slender needles, and does not melt on heating. T. A. H.

Aromatic Arsenic Compounds. II. Azo-dyes Containing Arsenic. P. KARRER (*Ber.*, 1912, **45**, 2359—2363. Compare this vol., i, 740).—The reaction of *p*-nitrosophenylarsinic acid, hydroxylamine hydrochloride, and *m*-tolylenediamine in aqueous sodium carbonate at 0° yields, after acidifying the solution, the red azo-dye, $C_6H_2Me(NH_2)_2\cdot N_2\cdot C_6H_4\cdot AsO(OH)_2$, which is produced by condensing diazotised arsanilic acid with *m*-tolylenediamine. *Azobenzene*-p-*arsinic acid*, $NPh:N\cdot C_6H_4\cdot AsO(OH)_2$, is an amorphous, brown powder obtained by the action of *p*-nitrosophenylarsinic acid on aniline

in boiling glacial acetic acid. *Azobenzene*-pp′-*diarsinic acid*, $AsO(OH)_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot AsO(OH)_2$, obtained in a similar manner from arsanilic acid and *p*-nitrosophenylarsinic acid, is a dark brown powder, which develops a purple-red coloration with concentrated mineral acids. *Bisazobenzene*-4 : 3′ : 4″-*triarsinic acid*,

$$AsO(OH)_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(AsO_3H_2)\cdot N_2\cdot C_6H_4\cdot AsO(OH)_2,$$

a black powder with green reflex, is similarly obtained from *p*-phenylenediaminearsinic acid. C. S.

Influence of Nuclear Alkyl Groups on the Mercuriation of Aniline and its Nitrogen Substitution Products. WALTER SCHRAUTH and WALTER SCHOELLER (*Ber.*, 1912, 45, 2808—2818).—In extension of previous work (Abstr., 1911, i, 699), the results of an investigation of the action of mercuric acetate on toluidines and their acyl derivatives are given.

[With JULIUS ROTHER.]—Molecular proportions of *o*-toluidine and mercuric acetate in methyl alcohol give rise to 15% of mercuri-*o*-toluidine, the chief product being a *diacetoxydimercuri*-derivative, $C_{11}H_{13}O_4NHg_2$, m. p. 228° (corr. decomp.), which crystallises in microscopic needles, is insoluble in most organic solvents, slightly soluble in methyl alcohol, but readily in ammonia or amines. On treatment with sodium hydroxide in water, it yields *dihydroxymercuri*-o-*toluidine*, long, colourless needles; this on warming at 100° loses H_2O, giving an infusible canary-yellow *substance*, which probably has the constitution

$$OH\cdot Hg\cdot C_6H_2Me{<}\begin{matrix}NH\\ |\\ Hg\end{matrix}.$$

The diacetoxymercuri-*o*-toluidine on acetylation in ethyl acetate solution gives *diacetoxydimercuriaceto*-o-*toluidide*, $C_{13}H_{15}O_5NHg_2$, m. p. 240° (corr.), from which by double decomposition with sodium chloride or bromide in water, the corresponding *dichloromercuri*-derivative, $C_9H_9ONHg_2Cl_2$, or *dibromomercuri*-compound,

$$C_9H_9ONHg_2Br_2,$$

may be obtained, crystallising in microscopic needles. *Di-iodomercuri-aceto*-o-*toluidide* is precipitated in flocks, but passes into a crystalline modification on keeping.

Mercury-*o*-toluidine was obtained as *chloromercuri*-o-*toluidine*, C_7H_8NHgCl, m. p. 178°, by adding sodium chloride to the mother liquor from which the diacetoxymercuri-compound had separated; it crystallises from dry alcohol in glancing needles, and on acetylation yields *chloromercuridiaceto*-o-*toluidide*, $C_{11}H_{12}O_2NHgCl$, m. p. 170° (corr.), in colourless leaflets.

Diacetoxymercuri-m-*toluidine* is more soluble in dilute alcohol than the ortho-isomeride, has no definite melting point, and yields an *acetyl* derivative. The corresponding dihydroxy-compound could not be obtained. *Triacetoxymercuri*-m-*toluidine*, $C_{13}H_{15}O_6NHg_3$, obtained by the action of mercuric acetate in excess on *m*-toluidine, forms bright yellow, microscopic crystals; the *acetyl* derivative is a colourless, heavy powder.

The acetyl derivatives of all three toluidines react with mercuric acetate in water, giving mono-substitution products. *Acetoxymercuri-*

aceto-o-*toluidide*, $C_{11}H_{13}O_3NHg$, m. p. 233° (corr.), forms needles. The meta-*isomeride*, m. p. 99° (corr.), crystallises from 30% alcohol, and the para-*compound*, m. p. 229° (corr.), crystallises in leaflets.

Ethyl *o*-toluidinoacetate gives a mono- or di-substitution product according to the concentration of mercuric acetate used. *Ethyl acetoxymercuritoluidinoacetate*, $OAc{\cdot}Hg{\cdot}C_6H_3Me{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, m. p. 122·5° (corr.), crystallises in needles, and on hydrolysis by alkalis gives *hydroxymercuri*-o-*toluidinoacetic anhydride*, $C_6H_3Me{<}\begin{matrix}NH{-}CH_2\\ Hg{\cdot}O{\cdot}CO\end{matrix}$, as a flocculent, colourless precipitate. *Ethyl diacetoxymercuri*-o-*toluidinoacetate*, $C_6H_2Me(Hg{\cdot}O{\cdot}Ac)_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, m. p. 167° (corr.), forms small, slender needles.

Ethyl *m*-toluidinoacetate forms *mono*- or *tri*-substitution *products*, depending on the concentration of mercuric acetate used. The first of these has m. p. 127·5° (corr.), and on hydrolysis gives *hydroxymercuri*-m-*toluidinoacetic anhydride*, which is yellow. *Ethyl triacetoxymercuri*-m-*toluidinoacetate*, m. p. 185° (corr.), is crystalline, and dissolves with difficulty in alcohol.

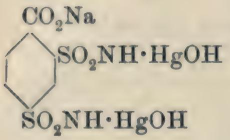
Ethyl *p*-toluidinoacetate gives only a mono-substitution *product*, m. p. 140° (corr.), which crystallises in small needles, and on hydrolysis yields *hydroxymercuri*-p-*toluidinoacetic anhydride* as a colourless, amorphous substance.

The position of the entering mercuric acetate was determined in certain cases by Dimroth's method (Abstr., 1902, i, 656); thus acetoxymercuriaceto-*o*-toluidide gives 5-iodoaceto-*o*-toluidide with iodine, whilst the diacetoxy-*m*-compound gives 4:6-di-iodoaceto-*m*-toluide; the former must therefore have its groups in the positions $CH_3{:}NH_2{:}Hg = 1:2:5$, whilst the second has its substituents arranged thus: $CH_3{:}NH_2{:}Hg{:}Hg = 1:3:4:6$. According to Pesci (Abstr., 1898, i, 648), *p*-toluidine takes up mercury in the *ortho*-position with respect to the amino-group. The *iodo*-compound, m. p. 222·5° (corr.), obtained from diacetoxymercuriacetyl-*o*-toluidine crystallises in long, silky needles. According to Holleman's rule the mercuric acetate residue should enter in the following positions with respect to the amino-group in the ethyl toluidinoacetates: *ortho*-ester, 4 and 6; *meta*-ester, 2, 6, and 4; *para*-ester, 2 (compare Abstr., 1911, i, 699). T. A. H.

Colloidal Acetate of Penta-mercuriacetanilide. M. Raffo and G. Rossi (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 120—121).—By heating together mercuric acetate and acetanilide in the molecular ratio 5:1, the authors have prepared the acetate of penta-mercuriacetanilide, having the composition $C_6(HgOAc)_5{\cdot}NHAc,2H_2O$. The mixture, impregnated with a little mercury, is heated for an hour at 115°, the temperature being then raised slowly to 145°, at which it is maintained for about half an hour. The resulting pasty mass is cooled, treated with a small quantity of boiling water, filtered, and the residue left for some hours in contact with cold water. The substance dissolves, giving a viscous solution which resembles egg-albumin. This solution coagulates at 80°, but the coagulum redissolves on cooling. If the solution is boiled for some time, the coagulum is no longer soluble in water. On addition of acetic acid to the viscous solution, needle-

shaped crystals of the above composition are slowly deposited. The colloidal character of the solutions which this substance yields is supposed to be connected with its high molecular weight. H. M. D.

Preparation of Readily Soluble Compounds of Oxymercurisalicyl Anhydride (Salicylic Acid Mercury Oxides). JOHANNES KERB (D.R.-P. 247625).—A description of complex soluble double salts of mercury with organic acids.



The *compounds* obtained from sodium *o*-hydroxymercurisulphaminobenzoate (1 mol.) and mercury salicylate (2 mols.), and from *sodium* 2 : 4-*dihydroxymercurisulphaminobenzoate* (a feebly basic powder) with mercury salicylate (4 mols.), are pale yellow powders, soluble in water, and decomposed by ammonium sulphide with separation of mercury. F. M. G. M.

Aluminium Triphenyl. SIEGFRIED HILPERT and GERHARD GRÜTTNER (*Ber.*, 1912, **45**, 2828—2832).—The preparation and properties of aluminium triphenyl are described. The substance was obtained by mixing mercury diphenyl with aluminium foil and heating to 140° in an atmosphere of dry hydrogen or nitrogen. The yellow, viscous mass thus obtained was boiled with ether and the solution evaporated in absence of air and moisture, when it deposited colourless needles, m. p. 112—113°, containing ether of crystallisation, which could only be removed by melting the product under reduced pressure. The ether-free *aluminium triphenyl* thus obtained forms masses of radiating needles, m. p. 196—200°, and cannot be distilled, even under reduced pressure. It explodes when heated in contact with cupric oxide, so that its carbon content could only be determined by a wet method. The compound is fairly stable when kept in compact masses in dry air. but when dry air is passed through a solution in ether, a colourless, amorphous precipitate, $AlOC_6H_5$ (?), is formed, along with some diphenyl.

With water, aluminium triphenyl reacts vigorously and the mixture is apt to take fire. The products are benzene, diphenyl, and alumina. With alcohol an infusible *product* is formed, which is decomposed by water, liberating phenol. Chloroform reacts with aluminium triphenyl, giving a yellow, semi-crystalline *product*, which is slowly decomposed by water with the separation of alumina and the liberation of some chloroform, but no triphenylmethane or the substances likely to accompany it could be detected. Carbon tetrachloride reacts similarly to chloroform. With iodine in ether, aluminium triphenyl reacts in the proportions necessary to give aluminium iodide and phenyl iodide, and a crystalline intermediate product separates. T. A. H.

Organic Chemistry.

Kachler's Ethylene-Ferrous Chloride. WILHELM MANCHOT and JULIUS HAAS (*Ber.*, 1912, **45**, 3052—3055).—Kachler (*Ber.*, 1869, **2**, 510) has described the compound $C_2H_4FeCl_2,2H_2O$, prepared by heating ferric chloride in ethereal solution with the addition of phosphorus in carbon disulphide in sealed tubes at 140—150°. The existence of this compound is improbable on theoretical grounds, and it is now shown to be an additive product of ferrous chloride and ether which has already largely decomposed before it can be analysed. Apparently the ferric chloride is reduced by the phosphorus, and the insoluble ferrous chloride at the moment of formation combines with ether and crystallises. E. F. A.

Bromine Absorptive Capacity of Organic Compounds. ISIDOR KLIMONT [in part, with WILHELM NEUMANN and E. SCHWENK] (*Arch. Pharm.*, 1912, **250**, 561—589).—A critical résumé is first given of the methods that have been proposed or used for determining the bromine absorption of organic compounds. The method adopted is that already described (this vol., i, 37; compare Mossler, *Zeitsch. allg. Österr. Apoth.-Ver.*, 1907, p. 225, and Gaebel, this vol., ii, 497). It has been applied to aliphatic, hydroaromatic, and aromatic substances, and the experimental results are given in the original. From these the following conclusions are drawn. The method gives erroneous results if hydrogen bromide is liberated, since this produces hydriodic acid when potassium iodide is added, which may act as a reducing agent and give rise to high bromine numbers. The high bromine numbers given by old turpentine oils are probably due to this cause. In presence of too much water, bromine may produce hydrobromic acid, and for this reason 50% sulphuric acid is used to liberate the bromine.

Aliphatic compounds containing a single ethylene linking and either one $-OH$ or $-CO\cdot OH$ group give normal results. In presence of two carboxyl groups the results are abnormal; thus, maleic acid combines easily with bromine, but the results are not quantitative, because part of the maleic acid is converted into fumaric acid, which takes up bromine much less easily in the cold. Similar trouble is experienced with citraconic, mesaconic, and aconitic acids.

The open-chain terpenes and their derivatives give abnormal results, because they readily undergo ring formation under these conditions or in some cases take up water, forming saturated compounds. Cyclic terpenes in which the ethylenic linking is not present in a "bridge," for example, dipentene and camphene, give normal results. A "bridge" between atoms in the para-position is unaffected, but one in the meta-position behaves as an ethylenic linking; thus, pinene absorbs four atoms of bromine, but the results are not quite quantitative, probably owing to partial displacement of the "bridge" to the para-position.

Phenol absorbs six atoms of bromine, three of which are liberated as

hydrogen bromide, and abnormal results are given by the phenol ethers and polyhydric phenols. Benzene derivatives with an ethylenic linking in the side-chain give normal results, but these are sometimes interfered with in the case of stereoisomerides.

Results are quoted showing that the method gives different but constant results for turpentine oils of different origins, and is capable of detecting sophistication in turpentine oil. T. A. H.

Acetylenic Compounds. Robert Lespieau (*Ann. Chim. Phys.*, 1912, [viii]. **27**, 137—189).—A résumé of work already published. Compare especially the following papers: Abstr., 1899, i, 184; 1905, i, 401, 566; 1907, i, 580; 1908, i, 125, 496; 1909, i, 205, 282, 691; 1910, i, 149; 1911, i, 347; this vol., i, 7, 331. T. A. H.

Theory of Racemisation, Substitution, and the Walden Inversion. Johannes Gadamer (*Chem. Zeit.*, 1912, **36**, 1327—1329).—The author gives a brief re-statement of his theory of racemisation (*Chem. Zeit.*, 1910, **34**, 1004).

With reference to the different behaviour of metallic hydroxides, some giving a normal hydrolysis, whilst others cause a Walden inversion, it is suggested that the effect in the first case is primarily due to the anion (with rapid action), and that in the second case the cation (with a relatively slow action) is the agent. In an inversion of a molecule CabcCl by treatment with silver hydroxide, it is supposed that the chlorine atom is first removed, when the remaining groups tend to distribute themselves evenly around the central carbon atom; on account of the acquired momentum, however, they overswing themselves and pass into the relatively opposite configuration to the original, when the hydroxyl group attaches itself.

In the additive reactions assumed by the theory to participate in the processes, the author's views differ from those of previous workers, in that the addition is supposed to occur, not directly at the asymmetric atom, but at the halogen atom, the groups of the molecule thus formed undergoing subsequent rearrangement. D. F. T.

Products of the Action of Sodium Alkyloxides on Acid Esters. Anastase Dambergis and Telem. Komnenos (*Ber. Deut. Pharm. Ges.*, 1912, **22**, 417—424).—When ethyl acetate is treated with a methyl-alcoholic solution of sodium methoxide, partial transformation into methyl acetate occurs without formation of ethyl acetoacetate. The latter substance is also not produced when ethyl-alcoholic sodium ethoxide reacts with ethyl acetate. Sodium acetate is the main product of the latter change.

The solid product of the action of sodium on ethyl acetate consists solely of ethyl sodioacetoacetate unmixed with sodium ethoxide. It is found to require considerably less acid for neutralisation than is expected. The difference is ascribed to the probable presence of the two isomeric compounds $CH_3\cdot C(ONa)\colon CH\cdot CO_2Et$ and

$$CH_3\cdot CO\cdot CH\colon C{<}^{ONa}_{OEt},$$

to the latter of which no alkaline action is attributed. H. W.

Bromoacetic Anhydride. WILHELM STEINKOPF (*Ber.*, 1912, **45**, 3136—3139. Compare Gal, *Compt. rend.*, 1870, **71**, 272).—*Bromoacetic anhydride* may be prepared by distilling bromoacetyl bromide with sodium bromoacetate, sodium acetate, or phosphoric oxide under diminished pressure. It is a colourless liquid, b. p. 133—135°/12·5 mm., which solidifies to a white, crystalline mass, m. p. 41—42°, and reacts with ethylene glycol, yielding the dibromoacetate, b. p. 176·5—177·5°/14 mm. (compare Vorländer, Abstr., 1895, i, 19).

F. B.

Action of Oxychlorides of Silicon on Sodium Salts of Fatty Acids. JOAQUIN E. ZANETTI (*J. Amer. Chem. Soc.*, 1912, **34**, 1598—1600).—Experiments are described which show that silicon oxychlorides react with sodium acetate, propionate, and butyrate, with the production of the corresponding anhydrides, together with sodium chloride and silica. The action of the silicon oxychlorides is therefore analogous to that of the oxychlorides of phosphorus, sulphur, and carbon.

E. G.

Direct Synthesis of the Glycerides. ITALO BELLUCCI (*Gazzetta*, 1912, **42**, ii, 283—305. Compare Abstr., 1911, i, 259, 416, 515).—[With D. BACHILLI and E. GARRONI.]—The author has investigated the formation of glycerides when glycerol is heated at 215—220° and 30—40 mm. with the equimolecular quantity of palmitic, stearic, or oleic acid. The progress of the esterification as heating is continued is represented in curves, and is similar in all three cases. Mixtures of mono-, di- and tri-glycerides are formed, and if the heating is continued after all the acid is combined, the quantity of monoglyceride tends to increase.

R. V. S.

Basicity of Acids Containing Alcoholic Hydroxyl Groups. II. GENNARO CALCAGNI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 343—349, 445—449).—In a former paper the author has recorded the variation of conductivity of solutions of these acids during neutralisation with ammonia (compare Calcagni and Bernardini, Abstr., 1911, ii, 1078). In the present paper similar experiments are described, the neutralisation being effected with glucinum hydroxide, which the author has already used for this purpose in the case of lactic acid (Abstr., 1910, i, 708). The conductivity curves show that glycollic, lactic, and hydroxy*iso*butyric acids form in each case two types of salts, the ratios between acid and base being $1:\frac{1}{2}$ and $1:1$ respectively, so that they act as dibasic acids. Malic acid is a tribasic acid, forming three salts in the proportions $1:\frac{1}{2}$, $1:1$, and $1:1\frac{1}{2}$. Tartaric acid forms three salts ($1:\frac{1}{2}$, $1:1$, and $1:2$), and is, therefore, tetrabasic. Citric acid forms four salts ($1:\frac{1}{2}$, $1:1$, $1:1\frac{1}{2}$, $1:2$), and is consequently tetrabasic. Hence the alcoholic hydroxyl groups of the fatty acids behave like carboxylic hydroxyl groups. It also appears that these acids give only normal salts with $Gl(OH)_2$, so that the complex salts of which the existence has been asserted are not formed in reality.

R. V. S.

Cerebronic Acid. PHŒBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 381—388).—This acid was discovered by Thudichum, who considered it to be an isomeride of stearic acid. Thierfelder, however, found that its formula is $C_{25}H_{50}O_3$, and that it contained one hydroxyl group. In the present research it was found to be normal α-hydroxypentacosoic acid, and in the hydrolysis mixture it occurs in the form of two isomerides, one dextrorotatory ($[\alpha]_D^{20} = +4{\cdot}16°$), and the other optically inactive. The two can be separated by fractional precipitation with lithium acetate.

W. D. H.

Free Acetoneoxalic [Acetylpyruvic] Acid and its Derivatives. OTTO MUMM and CLEMENS BERGELL (*Ber.*, 1912, 45, 3040—3051).—Ethylacetylpyruvate is readily obtained on condensing acetone with ethyl oxalate by means of sodium ethoxide (Claisen and Styles, Abstr., 1887, 917), but it has not been hydrolysed to the acid. It was sought to obtain this in a manner analogous to that followed with benzoylpyruvic acid (Mumm and Münchmeyer, Abstr., 1911, i, 79) by condensing 5-methyl*iso*oxazole with methyl sulphate to the α-methylimide of acetylpyruvonitrile, $CH_3\cdot CO\cdot CH_2\cdot C(:NMe)\cdot CN$, but the only degradation product obtained was acetylpyruvamide, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CO\cdot NH_2$. This is more conveniently prepared by the action of aqueous ammonia on ethyl sodioacetylpyruvate. The action of phenylhydrazine on this amide leads to phenylmethylpyrazolecarboxylamide, $CMe{<}\begin{matrix}CH-C\cdot CO\cdot NH_2\\ NPh\cdot N\end{matrix}$. The ammonium salt of ethyl acetylpyruvate loses water at room temperature to form the *α-imide* of *ethyl acetylpyruvate*, $CH_3\cdot CO\cdot CH_2\cdot C(:NH)\cdot CO_2Et$.

Acetylpyruvic acid is obtained without difficulty by hydrolysing ethyl sodioacetylpyruvate with 4*N*-sodium hydroxide for one and a-half hours and extraction of the acid with ether. It forms colourless prisms, m. p. 98°, and can be partly sublimed in a vacuum without decomposition. It gives a red coloration with ferric chloride in alcoholic solution. It is monobasic to methyl-orange, and dibasic to phenolphthalein. It reacts with hydroxylamine, forming 5-methyl*iso*oxazole-3-carboxylic acid, $CMe{<}\begin{matrix}CH\cdot C\cdot CO_2H\\ O-N\end{matrix}$. With benzaldehyde a *monobenzylidene* compound, $CH_3\cdot CO\cdot C(:CHPh)\cdot CO\cdot CO_2H$, is obtained; with aniline hydrochloride in aqueous solution, *acetylpyruvanilide*, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CO\cdot NHPh$, is obtained, whereas with aniline in alcohol the product is a *phenylimide*, $CH_3\cdot CO\cdot CH_2\cdot C(:NPh)\cdot CO_2H$. When excess of aniline is used, three molecules react and two molecules of water are eliminated.

Acetylpyruvic acid in ethereal solution reacts with dry ammonia to form the *ammonium* salt. When this is kept, water is eliminated and the ammonium salt of a pyridinedicarboxylic acid obtained, namely, 3-*acetyl*-4-*methylpyridine*-2 : 6-*dicarboxylic acid*,

$$COMe\cdot C{<}\begin{matrix}CMe{=}CH\\ C(CO_2H)\cdot N\end{matrix}{>}C\cdot CO_2H.$$

This gives an intense, orange-red coloration with ferrous sulphate.

When boiled with acetic acid or heated above its melting point, a carboxyl group is eliminated, forming 3-*acetyl*-4-*methylpyridine*-2(or 6)-*carboxylic acid*.

Benzylideneacetylpyruvic acid has m. p. 165—166°. The *a-phenylimide* crystallises in orange-yellow plates, m. p. 139°; it only gives a coloration with ferric chloride after a time. The isomeric *anilide* crystallises in large, pale yellow plates, m. p. 140—141°. It immediately gives a coloration with ferric chloride. A mixture of the two isomerides has m. p. 20—30° lower. The *compound*, $C_{23}H_{23}O_2N_3$, produced by interaction with 3 mols. of aniline, crystallises in pale yellow, long rods, m. p. 170° (decomp.). It gives a reddish-violet solution with concentrated hydrochloric acid.

3-*Acetyl*-4-*methylpyridine*-2:6-*dicarboxylic acid* crystallises in colourless prisms + Aq, m. p. 133°, or anhydrous, m. p. 175°. The *monocarboxylic acid* has m. p. 260°.

The *a-methylimide* of *acetylpyruvonitrile* has m. p. 68°, and has both acid and basic properties. It gives a red coloration with ferric chloride.

Acetylpyruvamide has m. p. 131—132° (decomp.). *Ethyl acetylpyruvate a-imide* crystallises in thin prisms, m. p. 36—38°.

E. F. A.

Physico-chemical Studies of Photographic Developers. II. Oxidation of Ferrous Ion in Presence of Oxalate Ion. NIKOLAI SCHILOFF and BORIS BERKENHEIM (*Zeitsch. Elektrochem.*, 1912, 18, 939—943).—Although potassium oxalate and ferrous sulphate in acidified aqueous solution are both unacted on by free oxygen, the gas is rapidly absorbed by solutions containing the two substances. When the oxalate is present in excess, the total amount of oxygen absorbed by a given solution is practically identical with that required for the complete oxidation of the ferrous salt. The quantity of oxalate present remains almost unchanged, the slight diminution actually observed corresponding with the small amount of oxygen absorbed in excess of that required by the ferrous salt.

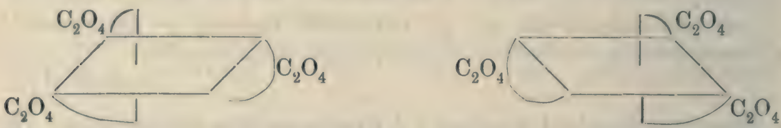
From observations on the quantity of oxygen absorbed by solutions in which the ratio of oxalate to ferrous salt was continuously varied, it is found that the molar ratio of oxalate to ferrous salt must be at least equal to three before complete oxidation of the ferrous salt is attained.

The facts can be explained on the assumption that the oxidisable substance is the complex ferro-oxalate ion, $Fe(C_2O_4)_2''$. On oxidation, this gives rise to the more stable ferri-oxalate ion, in which the ratio of oxalate to iron is as 3 : 1. Provided the solution contains oxalate in excess of this ratio, complete oxidation of the iron occurs, but if the proportion of oxalate is smaller, the oxidation of the ferro-oxalate ion will become impossible when a certain stage is reached, and the oxygen absorbed by such a solution will be less than that corresponding with the oxidation of the ferrous iron present. In accordance with this view, it is found that the addition of ferric sulphate to a given solution causes a large diminution in the quantity of absorbed oxygen. Furthermore, for a given ratio of oxalate to ferrous salt (this ratio being less

than 3) it is found that the quantity of oxygen absorbed increases with the dilution, which effect is probably due to the increasing dissociation of the complex ferri-oxalate ion. H. M. D.

Mirror Image Isomerism with Chromium Compounds. III. ALFRED WERNER (*Ber.*, 1912, 45, 3061—3070).—The optically active compounds hitherto obtained by the author (Abstr., 1911, i, 613, 838, 960; this vol., i, 10, 96, 298, 417) owe their activity to the presence of an optically active cation; they also contain nitrogen as one of the components of the cation. In the present paper optically active compounds are described containing an optically active anion, which does not contain nitrogen.

The blue trioxalochromiates (chromic oxalates) have the general formula $[Cr(C_2O_4)_3]R_3$, and contain tervalent chromium. Each oxalic acid residue is combined with the central chromium atom by means of a principal and a subsidiary valency, so that the compounds should show molecular asymmetry II, in accordance with the scheme:



When potassium barium trioxalochromiate, $[Cr(C_2O_4)_3]BaK$, is treated with the calculated quantity of dilute sulphuric acid, a solution of the potassium dihydrogen salt, $[Cr(C_2O_4)_3]KH_2$, is obtained. When a hot alcoholic solution of strychnine, in quantity sufficient to give the di-strychnine salt, is added to this solution, a light greyish-violet precipitate of potassium di-strychnine trioxalochromiate separates after a short time. This salt is readily recrystallised from 80% alcohol, and its aqueous solution is optically active, having $[\alpha]_G + 430°$. It shows a very pronounced rotation dispersion. The aqueous solution rapidly undergoes auto-racemisation, becoming inactive after one and a-quarter hours. The salt is soluble in aqueous acetone, and the solution is more stable than the one in pure water as solvent, and has $[\alpha]_G + 450°$.

When the potassium di-strychnine salt is recrystallised from hot water, the dilute hot solution deposits greyish-violet to slate-grey, leaf-like crystals of a totally different habit from those obtained from alcoholic solution. The aqueous solution of this salt, which is found to be tri-strychnine trioxalochromiate, is lævorotatory, $[\alpha]_G - 300°$; in aqueous acetone, $[\alpha]_G - 320°$. To account for this result it was supposed that the potassium di-strychnine salt first obtained was a mixture containing excess of the dextro-salt, but fractional recrystallisation disproved this. Further investigation showed that the mother liquors from which the salts separated were optically inactive, or practically so, but that on concentration further crops of the active salts were obtained.

The observed results can be explained on the assumption that the active salts are produced during the actual process of crystallisation, and that no partial racemates are formed in solution, bearing in mind the fact that auto-racemisation takes place very rapidly. In solutions

which have been warmed, or kept for some time, there are equal quantities of the potassium di-strychnine salt (*d*-acid) and potassium di-strychnine salt (*l*-acid), so that the solution is inactive. The former salt is sparingly soluble in alcohol, and crystallises out; auto-racemisation takes place rapidly in solution, giving fresh quantities of the *d*-salt, which crystallise out, and so on. The result is that an active salt is obtained, leaving an inactive mother liquor. In the case of aqueous solutions it is the *l*-salt which is least soluble, and consequently separates.

The auto-racemisation can be accounted for by assuming that one of the oxalic acid residues is only loosely combined with the chromium atom, and that in solution the linking is partly broken, so that rearrangement can take place. This is supported by the fact that the blue trioxalochromiates readily lose one oxalic acid residue.

That the anion is really optically active in the above salts is shown by the fact that when a paste of the potassium di-strychnine salt is triturated with solid potassium iodide, strychnine iodide is precipitated, leaving a bluish-violet solution from which alcohol precipitates potassium trioxalochromiate. The aqueous solution of this salt gives $[\alpha]_G$ $+1300°$, which is the highest specific rotation hitherto observed for a compound which has been isolated in the solid state, and is specially remarkable because of the comparative simplicity of the chromium-oxalic acid complex.

Potassium barium trioxalochromiate, $[Cr(C_2O_4)_3]KBa,2H_2O$, is obtained as a greyish-lilac precipitate when a solution of 20 grams of blue potassium trioxalochromiate in 100 c.c. of cold water is treated with 15 grams of finely powdered barium chloride. It forms strongly dichroic, greyish-lilac needles. *Potassium distrychnine trioxalochromiate* (*d*-acid), $[Cr(C_2O_4)_3]K(C_{21}H_{23}O_2N_2)_2,4H_2O$, prepared in the way indicated above, forms small, lilac-grey leaflets, with a pearly lustre. For recrystallisation the proportion of $1\frac{1}{2}$ grams of salt to 100 c.c. of alcohol (8 alcohol : 2 water) must not be exceeded, otherwise the active salt is mixed with racemate. In a three-field polarimeter the aqueous solution gives a greyish-violet middle field, the outer fields being orange in colour. In aqueous solution, $[\alpha]_G^9 + 430°$ and $[M]_G^9$ $+4719{\cdot}25°$, whilst in acetone solution (7 acetone : 3 water), $[\alpha]_G^{16}$ $+450°$, $[M]_G^{16} + 4937{\cdot}75°$.

Tristrychnine trioxalochromiate (*l*-acid), $[Cr(C_2O_4)_3](C_{21}H_{23}O_2N_2)_3,4H_2O$, prepared as indicated above, forms long, glistening leaflets, with a greyish-lilac shimmer. In aqueous solution, as also in aqueous acetone, $[\alpha]_G^9 - 330°$ and $[M]_G^{16} - 5016°$.

d-*Potassium trioxalochromiate*, $[Cr(C_2O_4)_3]K_3,H_2O$, forms a bluish-green, crystalline precipitate; in aqueous solution, $[\alpha]_G^9 + 1300°$ and $[M]_G^9 + 5637°$; in aqueous acetone, $[\alpha]_G^{16}$ $+1360°$ and $[M]_G^{16}$ $+5897°$. The l-*potassium trioxalochromiate*, $[Cr(C_2O_4)_3]K_3,H_2O$, is obtained from the tri-strychine salt by a method similar to that used for obtaining the *d*-potassium salt from the *d*-di-strychnine salt. In aqueous solution, $[\alpha]_G^9 - 900°$, $[M]_G^9 - 4336°$, and in aqueous acetone, $[\alpha]_G^{16} - 1000°$, $[M]_G^{16} - 4903°$. The rotation is less than that of the *d*-salt, because the preparation takes longer and auto-racemisation occurs to some extent.

T. S. P

Keto-enolic Tautomerism. VI. Relation between the Constitution and the Equilibrium of Keto-enolic Desmotropic Compounds. KURT H. MEYER (*Ber.*, 1912, 45, 2843—2864).—The author gives a résumé of the various chemical and physical methods of estimating the proportion of keto- and enolic modifications in a desmotropic compound, and is of opinion that his improved alcoholic bromine-β-naphthol process (Abstr., 1911, i, 832) is the best on account of its simplicity and convenience. A large number of desmotropic substances have been examined by this method, with the following important results. Any desmotropic substance which forms individual crystals is an individual compound; keto-enolic tautomerism is not exhibited by the crystallised substance. The modification in which a desmotropic substance exists in the crystalline state is not a criterion of its condition in the liquid or gaseous state; dibenzoylacetylmethane, which is ketonic in the solid state, is enolised to the extent of 98% in benzene, and methyl oxalacetate, enolic in the crystalline form, is present as the keto-form to the extent of 77% in alcohol.

In 3—5% solutions, an approximate proportionality has been observed between the equilibrium constants (that is, ratio of the concentration of the enolic to that of the ketonic modification) of desmotropic substances of allied constitutions and similar solubilities, in any given solvent. Thus the equilibrium constant of methyl benzoylacetate is about 2·2 times, and that of acetylacetone about 30—50 times, as great as that of ethyl acetoacetate in a given solvent.

Substances, such as acetaldehyde, acetone, acetophenone, or pyruvic acid, containing one ·COR group, do not contain an appreciable amount of the enolic modification, even in alcoholic solution in the presence of sodium ethoxide.

A comparison of substances containing a methylene group attached to two ·COR groups (where R may be H, Me, Ph, OH, OMe, OEt, NH_2, CO_2Me, or CO_2Et) shows that the percentage of the enolic modification, in a series of substances (in the liquid state or in alcohol) containing $\cdot CH_2\cdot COR$ in common, increases when the R's in the other ·COR group are arranged in the order OMe, OEt, OH, NHPh, Me, Ph, and CO_2Et (or Me); in other words, to give a specific example, a substance containing a benzoyl group has a greater tendency to enolise than a similarly constituted substance containing an acetyl group.

A similar regularity is not observed in compounds containing three substituents. The tendency to enolise of a substance, $CH_2(COR)_2$, is diminished when a methylene hydrogen atom is replaced by methyl, ethyl, or benzyl, and is, in general. increased when the hydrogen is replaced by another ·COR group. However, benzoylacetone is entirely enolic, whilst dibenzoylacetylmethane is entirely ketonic, in the crystalline states.

The author's bromine process confirms Wislicenus' statements regarding the isomeric modifications of ethyl formylphenylacetate (this vol., i, 623). The crystalline γ- and β-esters are entirely enolic; the liguid α-ester consists of 76% of enolic modification (or modifications) and 24% of the keto-form. C. S.

Keto-enolic Tautomerism. VII. Desmotropy of Malonic and Methanetricarboxylic Esters. KURT H. MEYER (*Ber.*, 1912, **45**, 2864—2869).—By the alcoholic bromine process, the authors show that (1) ethyl malonate does not contain the enolic modification; (ii) a few units % of the enolic modification are present when a solution of ethyl malonate in alcoholic sodium ethoxide is acidified, but do not persist for more than a minute; (iii) when a solution of ethyl malonate in methyl alcoholic sodium methoxide is added to a cold methyl alcoholic solution of bromine and hydrochloric acid, about 50% of the enolic modification is present. This proves that ethyl sodiomalonate has the constitution $CO_2Et\cdot CH\dot{:}C(ONa)\cdot OEt$, and that the free enol changes extremely rapidly to the keto-form.

Similar behaviour is shown by ethyl methanetricarboxylate. The crystalline substance is entirely the ketonic modification. Fused or in alcoholic solution, it contains about 0·2% of the enol. Its solution in methyl alcoholic sodium methoxide contains about 10% of the enol when acidified and treated immediately with alcoholic bromine, and about 80% of the enol when treated simultaneously with hydrochloric acid and the bromine solution.

The author shows that the bromination of malonic acid at 0° by aqueous bromine is independent of the concentration of the bromine. The reaction, therefore, as in the cases of acetone and ethyl acetoacetate, occurs in two stages, a slow change to the enolic form, followed by an immeasurably rapid addition of bromine. C. S.

Reaction between Maleic Acid and Sodium Thiosulphate. SEBASTIAN M. TANATAR and I. VOLJANSKY (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1320—1324. Compare this vol., i, 160).—The addition of sodium thiosulphate (1 mol.) solution to a solution of maleic acid (1 mol.) containing sulphuric acid (1 mol.) yields sodium sulphate and the *ester*, $CO_2Et\cdot CH(SH)\cdot CH(SO_2\cdot OH)\cdot CO_2Et$, which forms a viscous, yellow liquid and, on hydrolysis with hydrochloric acid, gives a mixture of the two acids: (1) $CO_2H\cdot CH(OH)\cdot CH(SO_2\cdot OH)\cdot CO_2H$ and

(2) $CO_2H\cdot CH(SH)\cdot CH(SO_2\cdot OH)\cdot OO_2H$,

the latter being converted into the former, with evolution of hydrogen sulphide, when heated in acid solution. In the pure state, acid (1) decomposes at 105°; its *silver*, $C_4H_3O_8SAg_3$, *barium*, and *calcium* salts were prepared.

Similar compounds were prepared by the action of potassium sulphite on fumaric and maleic acids by Credner (*Zeitsch. Chem.*, 1870, 77) and Messel (this Journ., 1871, 131) respectively, the latter author obtaining the acid, $CO_2H\cdot CH_2\cdot CH(SO_2\cdot OH)\cdot CO_2H$. T. H. P.

Condensation of Mercaptans with Formic Acid to Esters of Orthotrithioformic Acid. JOSEF HOUBEN (*Ber.*, 1912, **45**, 2942—2946. Compare Houben and Schultze, this vol., i, 5; Holmberg, Abstr., 1907, i, 474; this vol., i, 161).—The author has shown that methenyltrithiolacetic acid is formed by the action of formic acid on thioglycollic acid in the absence of condensing agents. He has also re-investigated the b. p. of ethyl orthotrithioformate, and, contrary to the experiments of Holmberg (*loc. cit.*), has confirmed the value previously found. H. W.

Thiolcamphoric Acid. M. M. Richter (*Ber.*, 1912, **45**, 3155—3156).—*Monothiolcamphoric acid*, $CO_2H\cdot C_8H_{14}\cdot CO\cdot SH$, prepared by warming a mixture of sulphur and sodium sulphide with camphoric anhydride, forms a viscous oil which readily decomposes, giving off hydrogen sulphide. The anhydride could not be obtained, camphoric anhydride resulting in its place. This was also formed instead of the expected disulphide on oxidation with iodine and potassium iodide in sodium carbonate solution. E. F. A.

r-Dilactylic Acid and *i*-Dilactylic Acid. Émile Jungfleisch (*Compt. rend.*, 1912, **155**, 799—804).—The crude dilactylic acid obtained by the action of the sodium derivative of ethyl lactate on ethyl α-chloropropionate (compare Abstr., 1907, i, 471) consists, for the most part, of the *r*- and *i*-acids, which are separated by means of their magnesium salts, that of the *i*-acid being the less soluble in cold water. After repeated crystallisation, *magnesium r-dilactylate*, $C_6H_8O_5Mg,6H_2O$, was obtained in colourless, voluminous prisms. The crystals exhibit marked birefraction, but inappreciable dispersion. The salt is soluble to the extent of 7—8 parts in 100 parts of cold water.

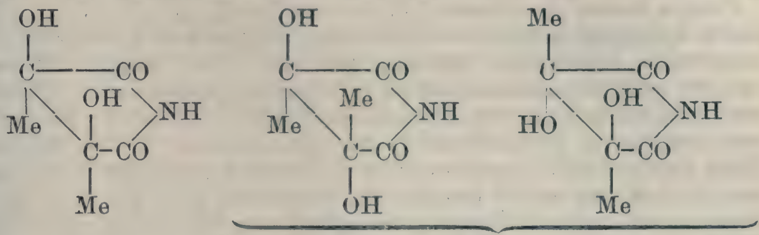
Magnesium i-*dilactylate*, $C_6H_8O_5Mg,3H_2O$, separates in small, grained crystals, with medium birefraction and high dispersive power. At 15°, 100 parts of water dissolve 2·28 parts of the salt. The optical characters of both these salts are given. The acids can be obtained from the salts by solution in dilute sulphuric acid, concentration in a vacuum, and extraction with ether, from which after evaporation the acids separate. The *r*-acid crystallises in large plates, m. p. 142°, and exhibits marked dispersion and strong birefraction. It can be resolved through its brucine salt. The *i*-acid separates in slender needles, m. p. 69—70°, which are hygroscopic. W. G.

Isomeric Diacetylcyanohydrins and their Transformation into the Imides of Dimethylmesotartaric Acid and Dimethylracemic Acid. Otto Diels and Paul Straumer (*Ber.*, 1912, **45**, 2946—2953).—According to Fittig, Keller, and Daimler (Abstr., 1889, 490), diacetyl combines with hydrogen cyanide to yield a dicyanohydrin, m. p. 110°. The authors find that this substance is transformed by warm nitric acid or hydrochloric acid into an isomeric cyanohydrin, m. p. 162°. Acetyl chloride transforms each into the same acetyl derivative, obviously on account of the transformation of the cyanohydrin of lower m. p. into that of higher m. p. by the liberated hydrogen chloride. Attempts to hydrolyse the two cyanohydrins are rendered difficult for a similar reason, but, under definite conditions, the authors have succeeded in obtaining different products of hydrolysis of the two substances, which they regard, however, as cyclic imides of the formulæ I and II (next page).

Saponification by alkali in the cold converts these substances into solutions which show differences similar to those observed with the two inactive modifications of tartaric acid.

Diacetylcyanohydrin, m. p. 110°, after softening at 108°, was obtained by the action of an anhydrous ethereal solution of hydro-

cyanic acid on diacetyl in the presence of potassium carbonate. When boiled with concentrated nitric acid (D 1·4) during one and a-half



(I.) (II.)

minutes, it was transformed into the *isomeride*, m. p. about 162°, after softening at 155°. The latter, when heated above its m. p., evolved hydrogen cyanide and diacetyl, which, on cooling, partly recombined to form the cyanohydrin, m. p. 110°. The latter was also obtained when a solution of the former in hot water was allowed to cool. Either cyanohydrin, on treatment with acetyl chloride and a trace of sulphuric acid, yielded the same *diacetyl* derivative, m. p. 172°.

The cyanohydrin, m. p. 110°, was hydrolysed by prolonged treatment with fuming hydrochloric acid at 40—42°. Among the products were ammonium chloride, the cyanohydrin, m. p. 162°, a *substance*, m. p. about 245° (decomp.) after previous softening, and the well-crystallised *imide*, m. p. 171°. When the latter was treated with zinc dust, unpleasant, basic vapours were evolved, which imparted a deep cherry-red colour to a pine shaving moistened with hydrochloric acid. The cyanohydrin, m. p. 162°, was hydrolysed under similar conditions, and an *imide*, m. p. 160°, obtained, which behaved similarly to the above imide on treatment with zinc dust.

Both imides were saponified by potassium hydroxide (33%). The product obtained from the imide, m. p. 171°, gave no precipitate with calcium chloride in weak acetic acid solution, and did not deposit crystals of an acid potassium salt when strongly acidified with the same reagent. In the same circumstances, the solution obtained from the imide, m. p. 160°, gave an immediate white precipitate with calcium chloride, and, after a short time, a crystalline precipitate when strongly acidified with acetic acid. H. W.

Hydrolysis of *l*-Acetylmalic Acid. BROR HOLMBERG (*Ber.*, 1912, **45**, 2997—3008).—In connexion with his views on the Walden inversion (this vol., i, 603), the author has submitted to careful examination the hydrolysis of *l*-acetylmalic acid.

l-Acetylmalic acid obtained by the method of Anschütz and Bennert (Abstr., 1890, 363) has m. p. 134—135°, $[\alpha]_D$ −10·71° (in water), whilst conductivity determinations give k 0·00237. The sodium salt in water has $[\alpha]_D$ −1·46°.

Hydrolysis of this substance by alkalis or acids gives malic acid of practically the rotation expected for the pure acid. It is therefore surmised that in the hydrolysis by either method, scission occurs at the valency attaching the Ac-group to the malic acid nucleus; if

scission occurred at the AcO-linking, racemisation or inversion would be expected.

From a kinetic consideration of the reactions it is deduced that the alkali hydrolysis should be bimolecular, but the acid hydrolysis unimolecular; experiment confirms this view, but wholly different velocity constants are observed for different concentrations or different alkalis in the first case, whilst in the second case the velocity constants are not directly proportional to the concentration of the hydrion. These discrepancies are explained by the effect of the cation in the first case, and in the second case by the suggestion that the acetylmalic ion undergoes hydrolysis much more rapidly than the undissociated acid.

In an addendum, the author replies to Senter's criticism (this vol., i, 828). D. F. T.

Mechanism of Oxidation Processes. HEINRICH WIELAND (*Ber.*, 1912, **45**, 2606—2615).—It has been shown previously (this vol., i, 248) that the catalytic oxidation of primary alcohols to aldehydes by finely divided metals of the platinum group is due to the activation of the hydrogen, which probably combines with the metal to form a hydride.

The further oxidation of aldehydes to acid appears to be due to a similar dehydrogenation of the aldehyde-hydrate, and not to the direct introduction of oxygen in the molecule, as is usually imagined: $CHR(OH)_2 \longrightarrow R{\cdot}CO_2H + H_2$.

This view is supported by the following facts: when moist acetaldehyde or benzaldehyde is shaken with palladium-black in the absence of air, acetic and benzoic acids are produced, together with hydrogen, which remains combined with the palladium. Admission of air to the reaction mixture causes the oxidation of the hydrogen to water. The oxidation of the hydrogen may also be effected by means of *p*-benzoquinone, methylene-blue, and other quinonoid compounds; thus moist acetaldehyde, when shaken with palladium and *p*-benzoquinone in the absence of air, is oxidised to acetaldehyde, the quinone being reduced first to quinhydrone and finally to quinol.

That the oxidation of aldehydes to acids by other oxidising agents really consists in the dehydrogenation of the aldehyde-hydrate is rendered very probable by the behaviour of acetaldehyde towards silver oxide. When perfectly dry these two substances do not react, although oxidation at once ensues if moist silver oxide is used. Further, chloral in benzene solution is oxidised only very slowly by silver oxide, whilst the hydrate suffers almost instantaneous oxidation.

The dehydrogenation of formaldehyde proceeds in a manner somewhat different from that of the aldehydes already mentioned. Formaldehyde at once reduces silver oxide with the formation of carbon monoxide and not of formic acid, as was to be expected from the behaviour of acetaldehyde and benzaldehyde; when passed over palladium-black, it is decomposed into carbon monoxide and hydrogen.

Although it is probable that the oxidation of aldehydes usually takes place by the dehydrogenation of an aldehyde-hydrate, the author agrees with Baeyer and Villiger (Abstr., 1900, i, 437) that the first phase in the autoxidation of aldehydes consists in the addition of

oxygen to the carbonyl group with the formation of a per-acid, which then reacts with a second molecule of aldehyde to form the corresponding acid.

The autoxidation of acetaldehyde and benzaldehyde is greatly accelerated by the presence of palladium, a result, no doubt, due to the adsorption of the oxygen by the finely divided metal, whereby the concentration of the oxygen is enormously increased. Quantitative experiments on the rate of oxidation of benzaldehyde by oxygen, both in the presence and absence of palladium, show that water has little effect on the velocity of oxidation; this is referred to the slow rate at which the dehydrogenation of the aldehyde-hydrate proceeds, as compared with the formation of acid by direct autoxidation. With acetaldehyde, on the other hand, the catalytic oxidation by palladium is retarded by the presence of water. The authors explain this result on the assumption that the concentration of the aldehyde is diminished, owing to the formation of the aldehyde-hydrate, which does not undergo autoxidation.

It is also mentioned that the first phase in the catalytic autoxidation of acetaldehyde by dry palladium consists in the formation of acetic anhydride.

It has been shown previously (this vol., i, 347) that the initial product of the combustion of carbon monoxide is formic acid, which then decomposes into carbon dioxide and hydrogen. Since carbon monoxide is an intermediate product in the combustion of coal gas in the bunsen flame, the author has examined the products for formic acid; cold water, on which a flame was allowed to impinge, was found to contain a small amount of formic acid. The acid was also identified in the air of rooms in which flames were burning and in the products of combustion of methane.

Under the influence of dry palladium at 250°, methane breaks down into carbon and hydrogen. When passed in a moist condition through a hot tube, it yields carbon dioxide and hydrogen.

The author also finds that carbon burns slowly in dry oxygen at 730°, thus confirming the observation of Baker (Abstr., 1889, 465).

F. B.

Preparation of Crystalline Zinc Formaldehydesulphoxylate. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248253. Compare Abstr., 1910, i, 40, and ii, 291).—The di-zinc salt of formaldehydesulphoxylic acid has been previously prepared, and the anhydride ("Decrolin") finds technical employment.

When a solution containing zinc formaldehydehyposulphite and zinc formaldehydesulphoxylate after concentration under reduced pressure is treated with alcohol, the former salt remains in solution, whilst zinc formaldehydesulphoxylate, $Zn(HSO_2\cdot CH_2O)_2$, separates in crystalline form; a 70% aqueous solution of this salt at 20° slowly deposits small, rhombic leaflets having the formula

$$Zn(HSO_2\cdot CH_2O)_2,4H_2O,$$

whilst a 100% aqueous solution at 60° furnishes the compound $Zn(HSO_2\cdot CH_2O)_2,3H_2O$ in glistening mother-of-pearl-like scales.

F. M. G. M.

Stereoisomerism of Trichloroacetaldoxime. F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 530—535. Compare Palazzo and Fazio, Abstr., 1911, i, 421).—As a result of experiments [with Egidi] shortly to be published, the author finds an explanation of the anomalies previously observed in regard to Meyer's chloraloxime in the fact that it is not an individual substance, but a mixture of two stereoisomerides. The decomposition with alkali is to be regarded as occurring as follows:

$$\begin{array}{c}HC\cdot CCl_3\\ \Vert\\ HO\cdot N\end{array} \longrightarrow \begin{array}{c}HC\cdot CO_2H\\ \Vert\\ HO\cdot N\end{array} \longrightarrow H_2O + HCN + CO_2.$$

$$\begin{array}{c}HC\cdot CCl_3\\ \Vert\\ N\cdot OH\end{array} \longrightarrow \begin{array}{c}HC\cdot CO_2H\\ \Vert\\ N\cdot OH\end{array} \longrightarrow \text{stable alkaline salt.}$$

R. V. S.

Synthesis of Alkyl Glucosides by the Action of Emulsin. β-*iso*Propyl Glucoside and β*iso*Amyl Glucoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 155, 854—857; *J. Pharm. Chim.*, [vii], 6, 442—445. Compare this vol., i, 790).—The glucosides were prepared by the general method already described (this vol., i, 672). β-iso*Propyl glucoside*, m. p. 123—125° (corr.), crystallises in colourless, odourless, hygroscopic needles, having a bitter taste. It is soluble in water, alcohol, and ethyl acetate, and has $[\alpha]_D$ $-36.3°$ in water. It has a very feeble reducing power, probably due to the presence of a small amount of dextrose. The synthesis is not so complete as in the case of its isomeride, β-propyl glucoside, thus showing an analogy with the esterification of the alcohols. β-iso*Amyl glucoside*, m. p. 99—100° (corr.), crystallises in colourless needles, having a disagreeable bitter taste; it is not hygroscopic, and does not reduce Fehling's solution; it has $[\alpha]_D$ $-36.4°$ in water. Both these glucosides are readily hydrolysed by emulsin in aqueous solution. W. G.

Synthesis of Alkyl Galactosides by means of Emulsin. β-Ethyl Galactoside. MILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1912, 155, 731—733; *J. Pharm. Chim.*, 1912, [vii], 6, 385—390. Compare Bourquelot and Bridel, this vol., i, 592, 672, 790).—β-Ethyl galactoside can be synthesised by the action of emulsin, obtained from almonds, on a 0·5% solution of galactose in alcohol (79—80%), kept at the rcom temperature for eighty-three days. So prepared, it crystallises in fine needles, m. p. 123—125°, and agrees in all respects, save its melting point, with the β-ethyl galactoside prepared by Fischer and Armstrong from β-acetylchlorogalactose (compare Abstr., 1902, i, 746). It is readily hydrolysed by sulphuric acid, or slowly by the same emulsin. Hydrochloric acid in alcoholic solution converts it into its α-isomeride. W. G.

The Preparation of Glucosides. WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 427—428).—Two methods for the preparation of glucosides were devised by Fischer; in the first, the alcoholic solution of the sugar is saturated with hydrochloric acid; this is neutralised with barium carbonate and removed as barium chloride. The large

expenditure of time required for repeated concentrations and extractions with alcohol led him to devise a second method, in which the sugar and alcohol are heated with a small amount of dry hydrochloric acid for thirty to fifty hours, and the acid removed by silver oxide, but the reaction occupies several days and is not complete. The following method is simple and gives a good yield in a day. The sugar and alcohol are treated with acid as in Fischer's first method. After an hour all reducing power disappears; the mixture is then concentrated to a quarter of its volume in a vacuum at 20°, and then poured into ordinary alcohol containing a little acetic acid. The excess of hydrochloric acid is removed by lead carbonate, and the filtrate after treatment with hydrogen sulphide is then concentrated in a vacuum and the glucosides isolated as usual. W. D. H.

The Behaviour of Starch under the Influence of the Silent Electric Discharge. Walther Löb (*Biochem. Zeitsch.*, 1912, **46**, 121—123).—One c.c. of 1% starch solution after the action of the discharge for two and a-quarter hours gives only a faint yellow colour with iodine solution, osazones can be formed, and the solution readily reduces Fehling's reagent. 0·5 Gram dissolved in 3 c.c. of water still yields a blue colour with iodine solution after four hours' action of the discharge; in this case the solution also yields osazones. Ten c.c. of 1% starch solution gives no reaction with iodine after three and a-quarter hours' treatment. S. B. S.

Influence of Temperature on Hydration of and Absorption of Alkali by Regenerated Cellulose. Clayton Beadle and Henry P. Stevens (*8th Intern. Congr. Appl. Chem.*, 1912, **13**, 25—38).—An investigation on the influence of temperature on the absorption of water and sodium hydroxide from aqueous sodium hydroxide solutions containing 1—25% sodium hydroxide by regenerated cellulose, the particular form of regenerated cellulose employed being a monofil of 360 denier made by the cuprammonium process.

It is found that, for any given temperature between 5° and 40°, a maximum hydration takes place, these maxima being greater the lower the temperature; the maximum for 0°, however, falls below that for 5°; at 5°, 12°, 20°, 30°, and 40°, maximum hydration takes place in about 9%, 10%, 10—11%, 11—12%, and 11—12% sodium hydroxide solution respectively, the amounts of water absorbed per 100 parts of regenerated cellulose at these maxima being roughly 2700, 1560, 920, 620, and 480 parts.

Similarly with regard to the absorption of sodium hydroxide, in which case maximum absorption at 5°, 12°, 20°, 30°, and 40° takes place in 9%, 10%, 11—12%, 12—14%, and 14% sodium hydroxide solution respectively, the maximum amounts of sodium hydroxide absorbed being 256, 162, 112, 82, and 78 parts respectively per 100 parts of regenerated cellulose.

The solution absorbed by the cellulose from dilute sodium hydroxide solutions between 0° and 40° is more concentrated than the unabsorbed or surrounding liquid, but for every given temperature there exists a certain concentration at which the absorbed solution has the same

composition as the surrounding solution; this point is somewhere about 6% for 0°, 8—9% for 20°, and 9—10% for 30°.

The effect of the addition of sodium chloride to the sodium hydroxide solution has also been investigated. It is found that the hydration of the cellulose varies but very slightly, increasing between 4% and 13% sodium hydroxide content, above which strength it slightly diminishes; at its maximum hydration (at 5°) it is never more than about one-tenth of the hydration observed in the absence of sodium chloride. The proportion of sodium hydroxide absorbed by the cellulose, however, becomes greater owing to the presence of the sodium chloride.

The addition of other soluble salts also alters the hydration and sodium hydroxide absorption in a marked degree. W. H. G.

Methylethylpropyl*iso*butylammonium *d*-Camphorsulphonate. EDGAR WEDEKIND (*Ber.*, 1912, **45**, 2940—2942. Compare Pope and Read, Trans., 1912, **101**, 519).—The author has made unsuccessful attempts to resolve methylethylpropyl*iso*butylammonium hydroxide by means of *d*-camphorsulphonic acid and *d*-bromocamphorsulphonic acid.

H. W.

Action of Metals on Alkyldichloroamines. ERWIN OTT (*Ber.*, 1912, **45**, 2922—2923).—According to Willstätter and Kahn, the action of finely-divided silver on dimethylchloroamine results in the formation of tetramethylmethylenediamine, $CH_2(NMe_2)_2$, and dimethylamine hydrochloride. The author shows that silver, zinc or magnesium have very little action on solutions of alkyldichloroamines in neutral solvents. Baeyer's "activated" magnesium reacts readily with ethereal solutions of dichloroamines, and yields the amines themselves after addition of water. Sodium reacts vigorously with a solution of ethyldichloroamine in xylene at 80—100°, with evolution of nitrogen, saturated hydrocarbons, and acetylene, and formation of sodium chloride and sodium acetylide. Methyldichloroamine behaves somewhat similarly, without, however, evolving acetylene.

β-Alkylhydroxylamines may be readily isolated as intermediate products in the reduction of alkyldichloroamines to amines in aqueous alkaline suspension by means of metals, alkali sulphides, etc.

H. W.

Preparation of a Therapeutically Valuable Derivative of Hexamethylenetetramine. EMANUEL MERCK and W. EICHHOLZ (D.R.-P. 247990).—When an alcoholic solution of hexamethylenetetramine is treated with an equimolecular proportion of glycocholic acid, the solution evaporated in a vacuum, and the syrupy product left in a desiccator, it hardens to a mass which can be pulverised and sinters at about 78°, decomposing without fusion at 100—103°.

F. M. G. M.

Some Derivatives of Choline. II. ROEMER R. RENSHAW (*J. Amer. Chem. Soc.*, 1912, **34**, 1615—1619).—[With F. G. FLOOD.]—Iodocholine iodide, m. p. 237·5° (corr.), can be obtained in 70% yield by leaving a solution of trimethylamine (1 mol.) and ethylene iodide

(1 mol.) in toluene for 6—8 days in sealed tubes. The *periodide*, $CH_2I\cdot CH_2\cdot NMe_3I,I_2$, forms long, dark reddish-brown, lustrous needles. Iodocholine *nitrate*, m. p. 183·5° (corr.), prepared by the interaction of iodocholine iodide and silver nitrate, crystallises in thin, lustrous plates, and when heated for twelve hours with an aqueous solution of silver glycerophosphate yields silver iodide, choline phosphate, glycerol, and some silver phosphate.

[With B. M. MacBride.]—Bromocholine bromide, m. p. 235·5° (corr.), can be obtained in 90% yield by heating ethylene bromide with trimethylamine in sealed tubes at 70—80°. The *nitrate*,

$$CH_2Br\cdot CH_2\cdot NMe_3\cdot NO_3,$$

m. p. 200° (corr.), crystallises in large plates. E. G.

New Compounds of the Choline Type. II. Acetyl Derivatives of α-Methylcholine, "β-Homocholine," and "γ-Homocholine." G. A. Menge (*J. Biol. Chem.*, 1912, **13**, 97—109).—The compounds described are prepared by heating the choline compound with a considerable excess of the acyl chlorides generally in a sealed tube at 100°. The reaction product is poured into dry ether, and the acyl derivative separated as an oily solid.

Acetyl-α-methylcholine is a slightly oily, crystalline, hygroscopic, white solid; the *platinichloride* forms a dense yellow, crystalline precipitate, m. p. 222—223° (corr.); the *aurichloride* is a pale yellow, crystalline solid, m. p. 124—125·5° (corr.).

Benzoyl-α-methylcholine forms a crystalline, hygroscopic solid; the *platinichloride* darkens above 233°, decomp. 236·5—237·5° (corr.); the *aurichloride* forms a pale yellow, very viscous oil.

Phenylacetyl-α-methylcholine is likewise an oil. The *platinichloride* has decomp. 245·7—246·7° (corr.).

Phenylacetyl-β-methylcholine is precipitated as an oily semi-solid product; the *platinichloride* has m. p. 216—217° (corr.). The *aurichloride* sinters above 60°, m. p. 74·5—76°, becoming limpid and clear at 85°.

Phenylacetyl-γ-homocholine separates as a colourless, flaky solid. The *platinichloride* crystallises in clusters of prisms, m. p. 193—194° (corr.); the *aurichloride* forms flaky crystals, m. p. 129—131° (corr.).

Propionyl-α-methylcholine forms a *platinichloride*, m. p. 231—232° (corr.).

Valeryl-α-methylcholine platinichloride sinters above 219°, decomp. with effervescence 228—229° (corr.); the *aurichloride* forms prisms, which sinter at 72°, m. p. 75°.

Monobromoisohexoyl-α-methylcholine platinichloride crystallises in clusters of very fine needles, decomp. 226—227° (corr.).

The *platinichloride* of *palmityl-α-methylcholine* decomp. 240—241°; the aurichloride has m. p. 72—75°. E. F. A.

Behaviour of the Amino-acids and Polypeptides to Neutral Salts. I. Paul Pfeiffer and J. von Modelski (*Zeitsch. physiol. Chem.*, 1912, **81**, 329—354).—The amino-acids and polypeptides form well characterised, crystalline compounds with neutral salts, which exist also in aqueous solution. They are obtained either by allowing an aqueous solution of the components to evaporate, or by adding alcohol and effecting crystallisation in closed vessels.

Glycine forms additive compounds with the chlorides and bromides of calcium, strontium, and barium of the type $CaCl_2,2NH_2\cdot CH_2\cdot CO_2H$, which are stable in the air. Calcium chloride also forms compounds with 1 and with 3 mols. of glycine; barium chloride, however, yields only one type of compound. Lithium chloride and bromide yield compounds with 1 and 2 mols. of glycine; lanthanum chloride combines with 3 mols. Alanine, glycylglycine, and diglycylglycine form similar additive compounds with calcium and lithium chlorides

These compounds are considered to have the constitution of salts both of the carboxyl and amine group, namely, $R<^{CO_2M}_{NH_3X}$, and are accordingly termed amphi-salts.

Glycine is more soluble in water in presence of neutral salts. The negative residues of the alkaline earth salts arranged in decreasing order of activity are as follows: $ClO_4 \longrightarrow NO_3 \longrightarrow Br \longrightarrow Cl \longrightarrow CO_2Me$. Calcium is more active than strontium or barium in increasing solubility.

It is considered that most of the protein salt complexes known are true chemical compounds.

Diglycine barium chloride, H_2O, forms large, transparent crystals with rhombic faces. It has not melted at 250°. The corresponding *bromide* forms characteristic, transparent plates, m. p. 180°.

Diglycine strontium chloride, $3H_2O$, separates in colourless, transparent, radially grouped crystals, which sinter at 75—80°. The *bromide* forms similar prismatic crystals, m. p. 94°, to a clear, viscid mass.

Diglycine calcium chloride, $4H_2O$, yields transparent, prismatic needles, m. p. 68°. The corresponding *bromide* forms colourless, flat needles without any definite melting point.

Diglycine magnesium chloride, $2H_2O$, forms tiny, colourless, intergrown crystals, which sinter at 215—220°.

Diglycylglycine calcium chloride gives anhydrous, transparent crystals of varying habit, which are not melted at 250°.

Glycylglycine lithium chloride crystallises in small, transparent needles.

Dialanine calcium chloride, $3H_2O$, forms colourless needles. E. F. A.

Losses in the Isolation of the Monoamino-acids by the Ester Method. III. Liberation of the Esters by means of Lead Hydroxide. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, 81, 226—227).—Zelinsky, Annenkoff, and Kulikoff (Abstr., 1911, i, 773) have described the preparation of the free amino-acid esters from their hydrochlorides by heating with excess of lead hydroxide. The method has been tested with alanine and glycine or with mixtures of both acids, but the yields obtained are very unsatisfactory. E. F. A.

The Possible Isomeric Tripeptides from the Three Monoaminocarboxylic Acids: Glycine, *d*-Alanine, and *l*-Leucine. EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1912, 81, 1—52).—The six possible tripeptides from glycine, *d*-alanine, and *l*-leucine have been synthesised by the ordinary methods. They differ only slightly in physical properties; this emphasises the difficulty of the identification of proteins. Mixtures of all six cannot be separated into the components.

The cell ferments (press juice from liver or pancreas, etc.) behave alike as regards the order in which they attack the tripeptides. Activated pancreatic extract behaves quite differently, attacking the compounds from the other end.

Chloroacetyl-d-*alanyl*-l-*leucine*, prepared from *d*-alanyl-*l*-leucine, $[\alpha]_D^{20} - 16{\cdot}96°$, crystallises in macroscopic needles in feather-like aggregates, m. p. 175°, $[\alpha]_D^{20} - 51{\cdot}58°$.

Glycyl-d-*alanyl*-l-*leucine* separates in macroscopic, slender, colourless needles, m. p. 239—240° (decomp.), $[\alpha]_D^{20} - 89{\cdot}85°$. The *copper* derivative is a bright blue, amorphous, glassy mass.

Chloroacetyl-l-*leucyl*-d-*alanine* forms colourless crystals, m. p. 136—137°, $[\alpha]_D^{20} - 41{\cdot}5°$.

Glycyl-l-*leucyl*-d-*alanine* crystallises in concentrically arranged needles of silky lustre, m. p. 235—236°, $[\alpha]_D - 59{\cdot}04°$. The *copper* derivative is reddish-violet in aqueous solution.

Chloroacetyl-l-*leucine* has m. p. 132—133°, $[\alpha]_D^{20} - 13{\cdot}82°$; the corresponding dipeptide has $[\alpha]_D - 35{\cdot}23°$.

d-*a*-*Bromopropionylglycyl*-l-*leucine* forms macroscopic, concentrically grouped needles or prisms, m. p. 152°, $[\alpha]_D^{20} + 14{\cdot}7°$.

d-*Alanylglycyl*-l-*leucine* separates in lustrous, silky needles, m. p. 243° (decomp.), $[\alpha]_D^{20} - 11{\cdot}2°$. The copper compound forms a vitreous blue mass, dissolving in water with an ultramarine-blue coloration. *l*-Leucylglycine has $[\alpha]_D^{20} - 84{\cdot}5°$.

a-d-*Propionyl*-l-*leucylglycine* crystallises in slender, intergrown needles, m. p. 154—155°, $[\alpha]_D^{20} - 24{\cdot}8°$.

d-*Alanyl*-l-*leucylglycine* forms needles, m. p. 246—247° (decomp.), $[\alpha]_D^{20} - 30{\cdot}43°$. The *copper* salt is greyish-blue and violet-red in aqueous solution.

d-*Alanylglycine* has $[\alpha]_D^{20} + 48{\cdot}33°$.

a-d-*Bromoisohexoyl*-d-*alanylglycine* yields stellate aggregates of needles, m. p. 129°, $[\alpha]_D^{20} - 2{\cdot}52°$.

l-*Leucyl*-d-*alanylglycine* crystallises in slender needles, which become brown at 244°, m. p. 252—253°. The copper compound is unique in being very soluble in absolute alcohol.

Glycyl-*d*-alanyl-*l*-leucine is hydrolysed by yeast juice to glycine and *d*-alanyl-*l*-leucine.

Glycyl-*l*-leucyl-*d*-alanine is hydrolysed in a similar manner to glycine and *l*-leucyl-*d*-alanine. The precise character of the products of hydrolysis of these two tripeptides by other ferment solutions could not be established.

d-Alanylglycyl-*l*-leucine is hydrolysed by activated pancreas extract to *d*-alanylglycine and *l*-leucine; all other enzymes convert it into *d*-alanine and glycyl-*l*-leucine.

d-Alanyl-*l*-leucylglycine is hydrolysed by all enzymes to *d*-alanine and *l*-leucylglycine.

l-Leucyl-*d*-alanylglycine gives *l*-leucyl-*d*-alanine with activated pancreas enzyme, and *d*-alanylglycine and *l*-leucine in all other cases.

Lastly, *l*-leucylglycyl-*d*-alanine gives glycyl-*d*-alanine and *l*-leucine with yeast extract, and *l*-leucylglycine and *d*-alanine with pancreas extract.

E. F. A.

Separation of Amino acids by means of the Carbamino-reaction. MAX SIEGFRIED and E. SCHUTT (*Zeitsch. physiol. Chem.*, 1912, 81, 260—273).—The carbamino-reaction for the separation of amino-acids has been tested under a variety of conditions (compare Siegfried and Schmitz, Abstr., 1910, i, 448). It is found that glutamic and aspartic acids are completely precipitated, glycine almost completely, and about four-fifths of the total leucine and asparagine. Glucosamine is also precipitated to the extent of 80%. Some 20—35% of the other monoamino-acids are precipitated as carbamino-derivatives; phenylalanine, however, which is very resistant to the carbamino-reagent (Siegfried and Neumann, Abstr., 1908, i, 379), only gives about 8% of precipitate. E. F. A.

Putrefaction Researches with *d*-Glutamic Acid and Studies on γ-Aminobutyric Acid. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1912, 81, 294—314).—Ackermann stated that in the putrefaction of glutamic acid mixed with sodium chloride, dextrose and Witte's peptone, γ-aminobutyric acid was found in small quantity. It is very doubtful if this originates from the glutamic acid, for in the present research no trace of it was found either when glutamic or pyrrolidonecarboxylic acid was employed. The question whether by biological (bacterial) agents, pyrrolidonecarboxylic can be converted into pyrrolidinecarboxylic acid was also investigated, but without decisive results. W. D. H.

Decomposition of Salts of Glutamic Acid on Heating their Aqueous Solutions and a New Optically Active Non-sugar. VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm*, 1912, 37, 1—17).—When aqueous solutions of glutamic acid are heated, two isomeric acids are formed, namely, *l*-glutimic acid, which predominates at lower temperatures, such as those customary in sap-boiling in the industry, and *dl*-glutimic acid, which is almost the sole product at temperatures above 200°. *l*-Glutimic acid forms colourless crystals, m. p. 162—163°, $[\alpha]_D - 9.9°$; when hydrolysed with hydrochloric acid the lævorotatory hydrochloride of glutamic acid is obtained. In similar conditions inactive glutimic acid yields the hydrochloride of *dl*-glutamic acid. *l*-Glutimic acid has been identified in molasses, where it is present to the extent of at least 3%. This causes an error of 1·23% in the determination of the sugar present by polarimetric methods. E. F. A.

The Copper Complexes of Amino-acids, Peptides, and Peptones. I. PHILIP A. KOBER and K. SUGIURA (*J. Biol. Chem.*, 1912, 13, 1—14).—A quantitative method is described for preparing copper salts of soluble amino-acids and peptides, of insoluble amino-acids having soluble copper salts, and insoluble amino-acids having insoluble copper salts. Some fifty of these compounds are described, and contain 1 atom of copper to one mol. of peptide. On an average, 99% of the copper of all amino-acid salts is precipitated as oxide when treated with a certain excess of alkali. In the case of peptide salts, the figure varies from 6·3 to 7·3%. W. D. H.

Copper Complexes of Amino-acids, Peptides, and Peptones. II. Their Configurations and Relation to the Biuret Reaction. PHILIP A. KOBER and K. SUGIURA (*Amer. Chem. J.*, 1912, 48, 383—411).—In an earlier paper (preceding abstract) it has been shown that monobasic α-amino-acids invariably form complex copper salts, CuA_2, and that the same is true of β-amino-acids except in cases, such as *iso*serine, in which there is an OH-group in the α-position. With dibasic amino-acids, such as glutamic and aspartic acids, compounds of the formula CuA are produced. Fischer has found that amino-acids with the NH_2-group in the γ-, δ-, or ϵ-position do not form complex copper salts whether there is an OH-group in the α-position or not.

The results of the examination of fifty polypeptides have now shown that 1 mol. of polypeptide combines with only 1 mol. of copper hydroxide. The imino-group alone does not seem sufficient to form a copper salt; thus bromo- or chloro-derivatives of dipeptides, as well as hippuric acid and formyl derivatives of amino-acids, all having an imino-group but no amino-group, do not form complex salts with copper hydroxide. On the basis of these facts and a consideration of the valency of protein nitrogen, a discussion is given of the possible configurations of the copper complexes.

A study has been made of the behaviour of the various classes of amino-acids towards the biuret reaction. It has been found that all simple dipeptides from monoamino-acids (excluding their amides) and their carboxyl derivatives give a deep blue colour with copper in alkaline solution. The neutral copper salts of all tripeptides from monoamino-acids and their carboxyl derivatives (amide derivatives excepted) and of all amides of dipeptides change colour on addition of excess of alkali and give "semi-biuret" colours, of shades varying with the constituent amino-acids and the temperature. The colour of the neutral copper salts of all tetrapeptides of monoamino-acids and of amides of tripeptides change on addition of excess of alkali from the deep blue of the neutral copper complex to the purple-red biuret colour. It seems that a true biuret reaction can only take place when four nitrogen atoms are so arranged that they can combine "co-ordinately" (in the sense in which the word is used by Werner) with the copper in an alkaline solution. A semi-biuret reaction can only occur when three nitrogen atoms are so arranged that they can combine co-ordinately with the copper in an alkaline solution. E. G.

Preparation of α-Bromo-α-ethylbutyrylcarbamide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249906).—It is found that α-bromo-α-ethylbutyrylcarbamide (Abstr., 1911, i, 118), m. p. 116—118°, can be more satisfactorily prepared as follows: (1) α-bromo-α-ethylbutyrylamide (100 parts) is dissolved in 500 parts of carbon tetrachloride, and treated with the requisite amount of cyanic acid and the mixture heated at 100° during five hours, or (2) from *α-bromo-α-ethylbutyrylcarbamyl chloride*, a colourless liquid, b. p. 90—98°/20 mm. (obtained by the action of phosphorus pentachloride on α-bromo-α-ethylbutyrylurethane), by the action of 10% ammonium hydroxide solution (3 parts) at a low temperature. F. M. G. M.

Preparation of Amides and Carbamides of Higher Bromo- or Iodo-fatty Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 248993).—The amides and carbamides of halogenated acids containing an eleven-carbon complex are found to be of therapeutic value, and to be readily prepared by ordinary methods.

Di-iodobrassidyl chloride crystallises from methyl alcohol; the *amide*, colourless aggregates, has m. p. 93°, and can also be prepared by treating *behenolamide* (m. p. 92°) at 60° during three hours with an acetic acid solution of iodine.

The *carbamide* of dibromobehenic acid forms colourless crystals, m. p. 149°, and the *amide*, a crystalline, colourless product, m. p. 78°. *Iodobehenamide* has m. p. 78°. F. M. G. M.

Thiocarbimides: Ethyl Allyliminothiolcarbonate. WILHELM SCHNEIDER (*Ber.*, 1912, **45**, 2961—2965).—The thiocarbimide of glucosides, for example, sinigrin, can be regarded as derived from a hypothetical alkyliminothiolcarbonic acid, NR⁚C(SH)·OH (Gadamer, Abstr., 1897, i, 360; 1898, i, 38). A derivative of this acid, namely, ethyl methyl phenyliminothiolcarbonate, NPh⁚C(SMe)·OEt, has already been prepared (Liebermann, Abstr., 1881, 44; 1882, 296); but as aromatic thiocarbimides apparently do not occur naturally, the author by a similar process has prepared the corresponding allylimino-compound.

[With GUSTAV HÜLLWECK.]—Allylthiourethane (Hofmann, *Ber.*, 1869, **2**, 117) treated in alcoholic solution with an equimolecular quantity of ammoniacal silver solution gives a yellow *silver* salt, C_3H_5·N⁚C(SAg)·OEt, m. p. 112—118°, which reacts with ethyl iodide in ethereal solution at 100°, producing *ethyl allyliminothiolcarbonate*, an oil, b. p. 88—92°/14 mm., of characteristic odour, which gradually decomposes when exposed to air and light. On boiling with an alkaline solution of lead oxide, no formation of lead sulphide occurs.

D. F. T.

Preparation and Properties of Pure Thiocyanic Acid. U. RÜCK and H. STEINMETZ (*Zeitsch. anorg. Chem.*, 1912, **77**, 51—89).—The method of Rosenheim and Levy (Abstr., 1907, i, 489) has been improved in detail, and an apparatus is described, but much decomposition of the product by the sulphuric acid occurs. Better results are obtained by using potassium hydrogen sulphate in place of sulphuric acid. For the preparation of pure gaseous thiocyanic acid, an apparatus is described in which purified and dried hydrogen enters a flask containing glass and porcelain balls, which can be agitated by means of a glass stirrer, together with potassium thiocyanate (1 mol.). Potassium hydrogen sulphate ($1\frac{1}{4}$ mol.) is added gradually through a side-tube. A vacuum of about 40 mm. is maintained. The gas evolved is free from sulphur dioxide, formic acid, or hydrogen sulphide. The yield, as determined by conversion into the white silver salt, is 20%. The method of Rosenheim and Levy always yields a coloured silver salt.

It is not possible to dry the materials so thoroughly that the product is quite anhydrous, the best result being a 97% acid. It is, therefore, necessary to dry the gas. Commercial phosphoric oxide

introduces impurities, but the pure compound is chemically indifferent, and Merck's preparation proves to be sufficiently free from impurities. The drying tubes are packed with this phosphoric oxide, arranged in about 20 layers in each tube, supported on glass wool. Condensation takes place in U-tubes cooled by solid carbon dioxide and alcohol. The solid product usually shows a very faint yellow tint. A special closed apparatus is described in which the solid thiocyanic acid may be weighed, dissolved in water, and precipitated by silver nitrate. The product proves to be pure.

The gas is stable, and only slightly poisonous. The solid is stable in dry hydrogen at $-15°$, and dissolves readily in water, alcohol, ether, or benzene. The yellow decomposition product is insoluble in benzene, but dissolves readily in alcohol. Cryoscopic measurements in benzene, nitrobenzene, and glacial acetic acid give results indicating a mixture of single and double molecules. C. H. D.

Iron Salts which Combine with Carbon Monoxide. Wilhelm Manchot [with Ernest Merry and Pierre Woringer] (*Ber.*, 1912, **45**, 2869—2879).—Little is known of the absorption of gases by iron compounds other than that present in the blood. Manchot and Friend (Abstr., 1908, ii, 375) have shown that cuprous chloride as such does not absorb carbon monoxide, but only in the form of a complex. The same is true of iron compounds. Hofmann's ferropentacyano-ammino-sodium, $[Fe(CN)_5NH_3]Na_3,6H_2O$, absorbs carbon monoxide in aqueous solution, the ammonia being replaced by carbon monoxide. The reaction is dependent on the temperature and concentration; thus a solution containing 0·022 mol. of the iron salt absorbs only about 12·5 litres of carbon monoxide after many hours at 0°, whilst a solution containing 0·0037 mol. absorbs 22·4 litres (per gram-atom of iron) at 21·2° in fifteen minutes. Since absorption of carbon monoxide does not occur in aqueous ammonia, but proceeds rapidly in acid solution, it seems that the reaction is one of dissociation:

$$Na_3Fe(CN)_5NH_3 \rightleftharpoons Na_3Fe(CN)_5 + NH_3,$$

the absorption of carbon monoxide being rapid under conditions favourable to the removal of ammonia.

Similar results have been obtained in experiments on the absorption of nitric oxide by the same iron compound. The iron compound does not absorb ethylene or acetylene, but slowly combines with one equivalent of oxygen, the iron being simultaneously oxidised to the ferric state.

Hofmann obtained the iron compound of the constitution given above by saturating a cold 25% aqueous solution of sodium nitroprusside with ammonia, and filtering the crystalline precipitate before the whole of the nitroprusside had disappeared. (The author finds the substance has the composition $Na_3[Fe(CN)_5NH_3],3H_2O$, after drying over calcium chloride.) A *disodium ammonium salt*,

$$Na_2(NH_4)[Fe(CN)_5NH_3],2H_2O,$$

is obtained when the mixture is kept for twenty-four hours, so that the whole of the nitroprusside enters into the reaction. The reaction between sodium nitroprusside and aqueous ammonia, therefore, is accompanied by reduction of the iron to the ferrous state and

proceeds according to the equation, $Na_2[Fe(CN)_5NO] + 3NH_3 + H_2O = Na_2(NH_4)[Fe(CN)_5 \cdot NH_3] + NH_4 \cdot NO_2$; ammonium nitrite has been detected in the solution. C. S.

*cyclo*Pentadiene. KARL VON AUWERS (*Ber.*, 1912, **45**, 3077—3080).—The refraction of a very pure specimen of *cyclo*pentadiene obtained by distillation at a low temperature under diminished pressure has been determined with the following results: n_α 1·45031, n_D 1·45418, n_β 1·46355, n_γ 1·47172, $D_4^{4 \cdot 1}$ 0·8190, at 4·1°.

A comparison of the dispersivity of this specimen with the values obtained by Stobbe and Reuss (this vol., i, 842), shows that *cyclo*pentadiene distilled under ordinary pressure is not so strongly polymerised, as has hitherto been supposed, and, consequently, the previously observed depression of the molecular refraction cannot be due to polymerisation (compare Auwers and Eisenlohr, Abstr., 1910, ii, 367, 561).

Thiophen, furfuran, and pyrrole resemble *cyclo*pentadiene in exhibiting a depression in their molecular refraction, and it would thus appear that this depression is characteristic of both iso- and hetero-cyclic ring-systems of the type $\begin{matrix} CH{:}CH \\ | \\ CH{:}CH \end{matrix}\!\!>\!X$ (where $X = CH_2$, S, O, NH). According to the author, the depression is to be referred not to a specific influence of the supplementary or subsidiary valencies, but to the group CH:CH·CH:CH, the position of which, in the five-membered ring, becomes fixed in such a manner as to lead to the neutralisation of the main and partial valencies. F. B.

Benzene Structure Reviewed from Thermochemical Standpoint. II. WILLEBRORD TOMBROCK (*Chem. News*, 1912, **106**, 201—202. Compare this vol., i, 842).—The heat of combustion of benzene may be accounted for by Kekulé's formula on the assumption that the thermal influence of the aromatic character is considerable, or by the centric formula on the assumption that the thermal influence of the aromatic character is negligible. G. S.

Thermochemistry of Benzene. H. STANLEY REDGROVE (*Chem. News*, 1912, **106**, 224—225).—In connexion with Tombrock's last communication (this vol., i, 842), the author gives further thermochemical calculations which show the untenability of Kekulé's formula for benzene, and are in favour of Baeyer and Armstrong's centric formula. T. S. P.

Observations on the Hydrogenation of Aromatic Compounds. HEINRICH WIELAND (*Ber.*, 1912, **45**, 2615—2617).—From his experiments on the catalytic hydrogenation of olefinic and aromatic compounds (this vol., i, 247) in the presence of colloidal palladium, the author has drawn the conclusion that unsaturated compounds which decolorise potassium permanganate may be catalytically hydrogenised. In reply to Willstätter and Hatt (this vol., i, 545), who maintain that no such relationship exists, the author points out that the difference in the rate of reduction of aromatic and olefinic compounds is so great

that under the conditions employed by him the former remain practically unchanged, whereas the olefines are more or less rapidly hydrogenised. Further, the permanganate reaction must be carried out under definite conditions in order that the above-mentioned relationship may be maintained.

Benzene is readily oxidised by a permanganate solution acidified with sulphuric acid, and may be catalytically reduced by palladium-black and hydrogen under the conditions employed by Willstätter and Hatt.

Palladium is less sensitive to retarding influences than platinum; the reduction of benzene by palladium and hydrogen still takes place, although with somewhat diminished velocity, in the presence of thiophen, which completely inhibits the hydrogenation by means of platinum. F. B.

Autoxidation of Benzenoid Hydrocarbons when Exposed to Light. HERMANN SUIDA (*Ber.*, 1912, 45, 2909—2910).—The author has shown that considerable quantities of peroxides of hydrocarbons are formed during the autoxidation of homologues of benzene. He considers that in the case of the autoxidation of phenanthraquinone in the presence of aromatic hydrocarbons (Benrath and von Meyer, this vol., i, 876), the former plays the role of a suitable "acceptor" by disturbing the equilibrium usually attained in the autoxidation of hydrocarbons, $R + O_2 \rightleftarrows RO_2$, by the removal of oxygen. H. W.

Isomeric Changes of Haloids Containing a Tertiary Radicle in the Molecule. A. I. LEPIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1165—1189).—After discussing the literature of the subject (compare Michael and Leupold, Abstr., 1911, i, 250, and others), the author describes his own experiments on α-bromo-α-phenyl-ββ-dimethylpropane, $CMe_3 \cdot CHPhBr$. From the results obtained he draws the conclusion that haloids, the molecule of which contains a tertiary radicle and in which the halogen is adjacent to the carbon atom combined directly with the tertiary radicle, at a sufficiently high temperature undergo isomeric change in two directions simultaneously: (1) the halogen atom and one of the hydrocarbon groups of the tertiary radicle change places, with the result that the carbon skeleton of the original compound is changed, and the corresponding tertiary isomeride formed; (2) the tertiary compound formed and also the original haloid, as far as the structures of the molecules allow, undergo transformations which are regarded as the result of successive changes of position between halogen and hydrogen atoms without change of the carbon skeleton.

*Phenyl*tert.*-butylcarbinol*, $CMe_3 \cdot CHPh \cdot OH$, prepared from benzaldehyde and magnesium *tert.*-butyl chloride, forms fine needles, m. p. 45°.

α-Bromo-α-phenyl-ββ-dimethylpropane, $CMe_3 \cdot CHPhBr$, forms a colourless liquid, b. p. 109°/10 mm., D_4^0 1·2563, D_4^{20} 1·2373, n_D^{20} 1·53977, which solidifies to a glassy mass when cooled in a mixture of solid carbon dioxide and ether.

The principal products obtained on heating this bromo-derivative for six hours in a sealed tube at 220° are: I. β-Phenyl-γ-methyl-Δ^{β}-

butylene (compare Blaise and Courtot, Abstr., 1906, i, 793), D_4^0 0·9080, D_4^{20} 0·8917, n_D^{20} 1·51635, which, when oxidised by means of benzoyl hydroperoxide, yields the corresponding *a-oxide*, $O<\begin{matrix}CMe_2\\ |\\ CMePh\end{matrix}$, in the form of a mobile liquid, b. p. 89—94°/8 mm., D_4^0 0·9976, D_4^{20} 0·9808, n_D^{20} 1·50757. Hydration of this oxide by prolonged treatment with water faintly acidified with sulphuric acid yields *β-phenyl-γ-methylbutylene βγ-glycol*, OH·CMe_2·CMePh·OH, crystallising from light petroleum in small needles, m. p. 84°, which do not distil. Oxidation of this glycol by means of chromic anhydride and potassium hydrogen sulphate yields acetophenone, and, possibly, a small proportion of acetone. II. A colourless liquid, $C_{11}H_{15}Br$, b. p. 116°/9 mm., D_4^0 1·2495, D_4^{20} 1·2304, n_D^{20} 1·54052, which is probably the tertiary isomeride of the starting product, that is, CMe_2Br·CHMePh, as it is found to be formed on bromination of the corresponding alcohol described below.

β-Phenyl-αα-dimethylpropyl alcohol, OH·CMe_2·CHMePh, prepared by the Grignard reaction from acetone and α-bromoethylbenzene, is a colourless, viscous liquid, b. p. 66°/0·09 mm., 105—107°/12 mm., D_4^0 0·9954, D_4^{20} 0·9794, n_D^{20} 1·51932, and is accompanied by two modifications of βγ-diphenylbutane (see succeeding abstract). Treatment of the alcohol with hydrogen bromide yields β-phenyl-γ-methyl-Δ^β-butylene and β-bromo-γ-phenyl-α-methylbutane (see above). T. H. P.

Stereoisomeric βγ-Diphenylbutanes (Dimethyldibenzyls). A. I. Lepin (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1190—1196).—The two dimethyldibenzyls obtained in the synthesis of β-phenyl-αα-dimethylpropyl alcohol (see previous abstract) have been obtained by Radziszewski (Abstr., 1874, 469), Engler and Bethge (Abstr., 1875, 65), Moritz and Wolffenstein (Abstr., 1899, i, 424), and Klages (Abstr., 1902, i, 666), but their structural relationship has not been ascertained. From their analogy to the tartaric acids, the author regards the liquid modification as the racemic mixture of the two enantiomorphous forms, and the solid one as the internally compensated form. Both give acetophenone on oxidation, and the former is converted into the latter when heated with a crystal of iodine in a sealed tube at 235—250°.

The solid modification forms white crystals, m. p. 126°, whilst the liquid modification has b. p. 140°/10 mm., 283—284°/752 mm., m. p. 8°, D_4^0 0·9906, D_4^{20} 0·9757, n_D^{20} 1·55516; both have about the normal molecular weight in freezing benzene. T. H. P.

Crystals of 1-Bromo-2 : 4-dinitrobenzene and Mixed Crystals of 1-Bromo- and 1-Chloro-2 : 4-dinitrobenzene. A. K. Boldyreff (*Zeitsch. Kryst. Min.*, 1912, 51, 294—295; from *Ann. Inst. Mines, St. Petersburg*, 1908, 1, 20—27).—Two-circle measurements and optical determinations are given for crystals of 1-bromo-2 : 4-dinitrobenzene and of mixed crystals (50%) of 1-bromo- and 1-chloro-2 : 4-dinitrobenzene. Although the optical orientation agrees with orthorhombic symmetry, the crystals are regarded as belonging to "the rhombo-prismatic kind of monoclinic syngony." L. J. S.

2:4:6-Trinitrobenzyl Bromide and its Derivatives. SIEGMUND REICH, OTTO WETTER, and MAX WIDMER (*Ber.*, 1912, 45, 3055—3061).—2 : 4 : 6-Trinitrobenzyl bromide is readily obtained by heating 2 : 4 : 6-trinitrotoluene with bromine under pressure (compare Reich, this vol., i, 361). It condenses readily in benzene solution with two molecules of aromatic amine; the toluidines, *o*- and *p*-anisidine, and *m*-nitroaniline, but not *o*- and *p*-nitroaniline, react in this manner. Anthranilic acid readily condenses with trinitrobenzyl bromide, so that the behaviour of the nitroanilines is due to the position of the nitro-groups and not to their acid character. The amines mentioned show the same differences when condensed with 2 : 4 : 6-trinitrobenzaldehyde, with which *o*- and *p*-nitroaniline do not react.

A by-product of the bromination of trinitrotoluene is hexabromobenzene.

2 : 4 : 6-*Trinitrobenzyl bromide* crystallises in colourless, glistening platelets, m. p. 67°.

2 : 4 : 6-*Trinitrobenzyl iodide*, prepared by action of the bromide on potassium iodide, forms brown, stunted crystals, m. p. 86—87°.

2 : 4 : 6-*Trinitrobenzyl alcohol* is obtained in short, brown needles, m. p. 100°, on prolonged boiling of the bromide with water.

2 : 6-*Dinitrobenzyl alcohol* crystallises in well-formed, slightly brown platelets, m. p. 94°.

2 : 4 : 6-*Trinitrobenzylaniline* forms brown needles, m. p. 151°.

2 : 4 : 6-*Trinitrobenzyl*-o-*anisidine* crystallises in reddish-yellow needles, m. p. 183°.

2 : 4 : 6-*Trinitrobenzyl*-p-*anisidine* yields dark brown needles, m. p. 143°.

2 : 4 : 6 - *Trinitrobenzyl-β-naphthylamine* gives brown needles, m. p. 150°.

2 : 4 : 6 - *Trinitrobenzyl*-o-*toluidine* forms orange-yellow needles, m. p. 140°.

2 : 4 : 6-*Trinitrobenzyl*-p-*toluidine* yields brown needles, m. p. 122°.

2 : 4 : 6-*Trinitrobenzyl*-m-*nitroaniline* forms red needles, m. p. 133°.

2 : 4 : 6-*Trinitrobenzyl*-o-*aminobenzoic acid* gives yellow needles, m. p. 170°.

2 : 6 : 2′ : 6′-*Tetranitrostilbene*, $C_6H_3(NO_2)_2\cdot CH\vdots CH\cdot C_6H_3(NO_2)_2$, prepared by the action of alcoholic potassium hydroxide on dinitrobenzyl bromide, crystallises in short, faintly yellow needles, m. p. 250°.

On reduction, *tetra-aminostilbene* was obtained in lustrous, colourless crystals, m. p. 164—166°, but not sufficiently pure for analysis.

2 : 4 : 6 : 2′ : 4′ : 6′-*Hexanitrostilbene* from trinitrobenzyl bromide forms yellow needles, m. p. 211° (decomp.). E. F. A.

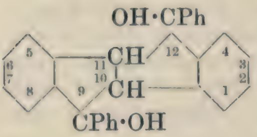
Preparation of a Monosulphonic Acid of Acenaphthene. KALLE & Co. (D.R.-P. 248994).—Di- and tri-sulphonated derivatives of acenaphthene have been prepared previously, and a monosulphonic derivative containing the sulphonic radicle in the methylene group has now been obtained as follows.

Acenaphthene (15·4 parts) dissolved in nitrobenzene is slowly treated at 3° with chlorosulphuric acid (12 parts), the temperature is

allowed to rise to 15—20°, and the mixture vigorously stirred for some time. The *sodium* salt forms colourless, crystalline leaflets.

F. M. G. M.

Coloured Hydrocarbons of the Diphensuccindene Series. I. KURT BRAND (*Ber.*, 1912, 45, 3071—3077).—Roser's (Abstr., 1888, 1301) diphensuccindone (diphensuccindan-9 : 12-dione) reacts with magnesium phenyl bromide, yielding 9 : 12-*dihydroxy*-9 : 12-*diphenyldiphensuccindane* (annexed formula), which crystallised in stout, colourless needles, m. p. 232—234°, with previous darkening, and is converted by heating with acetic, formic or mineral acids into 9 : 12-*diphenylsuccindadiene*,



$C_6H_4<\begin{matrix}C{:}CPh\\ CPh{:}C\end{matrix}>C_6H_4$ or $\begin{matrix}C_6H_4{:}C\cdot CPh.\\ CPh—C{:}C_6H_4\end{matrix}$ This forms lustrous, brown crystals, m. p. 259—260°, which become strongly electric when rubbed, and are oxidised by potassium permanganate or chromic acid to *o*-benzoylbenzoic acid.

9 : 12-*Dihydroxy*-9 : 12-*di*-p-*tolyldiphensuccindane*, $C_{30}H_{26}O_2$, prepared in a similar manner from magnesium *p*-tolyl bromide, forms colourless crystals, which become brown and melt at 248—250° ; when boiled with a mixture of formic and acetic acids it yields 9 : 12-*di*-p-*tolyldiphensuccindadiene*, $C_{30}H_{22}$, which separates from benzene in almost black crystals, having a metallic lustre.

The author mentions that Roser's diphensuccindone dissolves in aqueous sodium hydroxide, forming solutions of an orange colour, and suggests that the constitution of the sodium salt thus produced is represented by one of the following formulæ :

$$C_6H_4<\begin{matrix}C{:}C(ONa)\\ C(ONa){:}C\end{matrix}>C_6H_4 \qquad \begin{matrix}C_6H_4{=\!=}C\cdot C\cdot ONa\\ C(ONa)—C{:}C_6H_4\end{matrix}$$

F. B.

Condensation of Organic Compounds with the Aid of Iodine. KNOLL & Co. (D.R.-P. 250236).—The catalytic action of iodine has recently been demonstrated (this vol., i 345) and the following extension is now recorded.

A quantitative yield of dimethylaniline is obtained by heating aniline (93 parts), methyl alcohol (96 parts), and iodine (1 part), together during seven hours at 230° ; the analogous preparation of diethylaniline with ethyl alcohol requires ten hours' heating at 235°.

Di*iso*amylaniline is obtained from aniline and *iso*amyl alcohol after ten hours at 240° ; aniline (140 parts), methyl alcohol (32 parts), and iodine (1 part) after heating during ten hours at 220° furnishes chiefly methylaniline, whilst molecular proportions of aniline and *p*-benzophenone with 1% iodine yield (at the temperature of water elimination) benzophenoneanil ; and acetophenone with 1% iodine at 180—190° gives s-*triphenylbenzene*, m. p. 169—170°. F. M. G. M.

Reactions of Certain Fumaroid and Maleinoid Compounds with Aromatic Amines. WILLIAM H. WARREN and M. R. GROSE (*J. Amer. Chem. Soc.*, 1912, **34**, 1600—1613).—Perkin (Trans., 1881, **39**, 561) has shown that when an aqueous solution of aniline maleate is evaporated, a derivative of succinimide is produced. Anschütz and Wirtz (Abstr., 1887, 934) have found that the compound is anilinosuccinanil, $\begin{matrix} CH_2\cdot CO \\ NHPh\cdot CH—CO \end{matrix}\!\!>\!NPh$. It is now shown that both fumaric and maleic acids react with aniline to form anilinosuccinanil, and that in the production of this compound, two reactions are concerned, one leading to the formation of the imido-ring, and the other involving addition of the amine. These two reactions do not take place simultaneously, but the addition of the amine seems to depend on the presence of the imido-ring. It has been found that β-naphthylamine, *o*-, *m*- and *p*-toluidine, 2 : 4-xylidine, benzidine, benzylamine, and *p*-phenetidine resemble aniline in their behaviour towards fumaric acid, whilst tribromoaniline, *p*-bromoaniline, and methyl *p*-aminobenzoate fail to react.

Methyl hydrogen fumarate, $CO_2Me\cdot CH\colon CH\cdot CO_2H$, m. p. 143°, obtained by the partial hydrolysis of dimethyl fumarate, forms flattened prisms.

Anilinosuccinanil can be obtained by the action of aniline on methyl hydrogen fumarate, dimethyl fumarate, diethyl fumarate, or fumaric acid; it separates from alcohol in white crystals, and from glacial acetic acid in yellow crystals.

β-Naphthylaminosuccino-β-naphthylimide,

$$C_{10}H_7\cdot NH\cdot C_4H_3O_2\colon N\cdot C_{10}H_7,$$

m. p. 250—255° (decomp.), separates in yellow needles from glacial acetic acid, and in white crystals from acetone or alcohol; its *nitroso*-derivative, $C_{10}H_7\cdot N(NO)\cdot C_4H_3O_2\colon N\cdot C_{10}H_7$, m. p. about 260°, forms rhombic crystals.

o-*Tolylaminosuccino*-o-*tolylimide*, m. p. 112—113°, crystallises in white needles; its *nitroso*-derivative has m. p. 85°. The corresponding m- and p-*tolyl* compounds have m. p. 130° and 209—211°, and their *nitroso*-derivatives, m. p. 120° and 169—170° respectively.

2 : 4-*Dimethylphenylaminosuccino*-2 : 4-*dimethylphenylimide*, m. p. 132—133°, crystallises in pale yellow needles; its *nitroso*-derivative has m. p. 80—90°.

Experiments were made on the behaviour of fumaric acid towards *p*-phenylenediamine, but the result was not satisfactory. With benzidine, the *compound*, $\begin{matrix} C_6H_4\cdot NH \\ C_6H_4—N \end{matrix}\!\!>\!C_4H_3O_2$, was obtained which does not melt below 300°.

By the action of fumaric acid or ethyl fumarate on benzylamine, *benzylaminosuccinobenzylimide*, $CH_2Ph\cdot NH\cdot C_4H_3O_2\colon N\cdot CH_2Ph$, m. p. 205°, is produced which forms slender, white needles; its *nitroso*-derivative has m. p. 156°. p-*Ethoxyphenylaminosuccino*-p-*ethoxyphenylimide*, $OEt\cdot C_6H_4\cdot NH\cdot C_4H_3O_2\colon N\cdot C_6H_4\cdot OEt$, m. p. 204—205°, from *p*-phenetidine, forms slender needles; the *nitroso*-derivative has m. p. 133—134°.

By the interaction of fumaric acid (1 mol.) and methylaniline (3 mols.), *fumaromethylanilide*, NPhMe·CO·CH:CH·CO·NPhMe, m. p. 187—188°, is produced, which is identical with the compound obtained by Piutti (Abstr., 1886, 621) by the action of methylaniline on phthalylaspartic acid. It combines with bromine to form *dibromosuccinomethylanilide*, m. p. 214°, which forms short, hexagonal prisms.

When maleinanil (1 mol.) is heated with methylaniline (1 mol.), *methylanilinosuccinanil*, $NPhMe\cdot C_4H_3O_2{:}NPh$, m. p. 173°, is produced, which crystallises in long needles.

Fumarodiphenylamide, $NPh_2\cdot CO\cdot CH{:}CH\cdot CO\cdot NPh_2$, m. p. 272—273°, obtained by the action of fumaryl chloride on diphenylamine, crystallises in white, slender needles, and is identical with the compound obtained by Piutti (*loc. cit.*) from diphenylamine and fumaric or maleic acid. The substance combines with bromine to form *dibromosuccinodiphenylamide*, $NPh_2\cdot CO\cdot CHBr\cdot CHBr\cdot CO\cdot NPh_2$, m. p. 231°, which crystallises in white, slender needles.

Diphenylmaleinamic acid, $NPh_2\cdot CO\cdot CH{:}CH\cdot CO_2H$, m. p. 130°, obtained by the action of maleic anhydride (1 mol.) on diphenylamine (2 mols.), crystallises in radiating needles. E. G.

Condensation of Formaldehyde with Aniline. ALEXANDER M. NASTUKOFF and V. I. MALKALN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1196—1200).—The product previously obtained (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1125) by the condensation of formaldehyde with aniline in presence of conncentrated sulphuric and acetic acids is shown to consist of a mixture in approximately equal proportions of an imine closely resembling that described by Orloff (Abstr., 1906, i, 420) and of *aminobenzo*cyclo*butadiene*, $\begin{array}{l} CH{:}C(NH_2)\cdot C—CH \\ | \qquad\qquad\quad \Vert \quad \Vert \\ CH{=\!=\!=}CH\cdot C—CH \end{array}$. This was not obtained in the pure state, but when diazotised in alcoholic solution was found to yield a small proportion of a hydrocarbon, b. p. 104—107°, which is regarded as *benzo*cyclo*butadiene*, $\begin{array}{l} CH{:}CH\cdot C—CH \\ | \qquad\quad\; \Vert \quad \Vert \\ CH{:}CH\cdot C—CH \end{array}$.

T. H. P.

Condensation of Formaldehyde with *o*-Toluidine. ALEXANDER M. NASTUKOFF and P. M. KRONEBERG (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1200—1202).—Condensation of formaldehyde with *o*-toluidine in presence of concentrated sulphuric and acetic acids (compare *J. Russ. Phys. Chem. Soc.*, 1904, 36, 1125) yields as sole product, 6-*amino*-5-*methylbenzo*cyclo*butadiene*, $\begin{array}{l} CMe{:}C(NH_2)\cdot C—CH \\ | \qquad\qquad\qquad \Vert \quad \Vert \\ CH{=}CH{-\!-\!-}C—CH \end{array}$, which has the normal molecular weight in boiling pyridine. T. H. P.

Preparation and Decomposition of Benzylmonochloro- and Benzyldichloro-amines. RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1912, 34, 1613—1615).—It has been shown in an earlier paper (Trans., 1912, 101, 169) that dichlorocarbamide behaves as a chlorinating agent, and is capable of converting benzylamine into either the monochloro- or dichloro-amine according to the proportion used. The monochloroamine is slowly but quantitatively decomposed by water

with formation of benzaldehyde. The dichloro-compound also yields benzaldehyde under the same conditions, but the change is very slow. When dichlorobenzylamine is left in a stoppered bottle, it gradually changes into a solid crystalline mass consisting of benzoic acid.

E. G.

The Two Isomeric Trinitro-*p*-anisidines and a Trinitro-*p*-phenetidine. FRÉDÉRIC REVERDIN (*Arch. Sci. phys. nat.*, 1912, [iv], 34, 330—338. Compare Abstr., 1910, i, 470).—The constitution of the trinitro-*p*-anisidine of Meldola and Kuntzen (Trans., 1910, 97, 456) and of that prepared by Reverdin (Abstr., 1910, i, 470) is discussed, with particular reference to the position of the mobile nitro-group. Meldola's 2 : 3 : 5-trinitro-compound was obtained from a 3 : 5-dinitro-derivative, but it is suggested that the mobile group might have been displaced in the final nitration, for a trinitrophenol derived from the product resembles a known 2 : 3 : 6-trinitrophenol. Reverdin, who relies on Meldola's formula to establish his isomeric 2 : 3 : 6-trinitro-*p*-anisidine, could not succeed in methylating this compound or in causing it to condense with chloronitrobenzene, and assumes, therefore, that the amino-group is protected by two nitro-groups in the ortho-position. Similar inactivity in the case of the 2 : 3 : 5-compound is attributed by Meldola to the mobility of the nitro-group in position 3. That the mobile nitro-group does occupy position 3 in each case was shown by the formation of 2 : 6- and 2 : 5-dinitro-methoxybenzoquinonediazides (Trans., 1910, 97, 1204), and is now supported in the case of Reverdin's compound, by the fact that the reduction of the corresponding hydroxyl compound after elimination of the amino-group, yields a *m*-diamine, and further by the production of an *o*-diamine by the action of alcoholic ammonia. It is hoped to find more direct proofs of the mobility of this nitro-group, among others the conversion of the substance into a known dinitroresorcinol.

An improved method for the preparation of this trinitro-*p*-anisidine is found in the nitration of 4-*p*-toluenesulphonylanisidine in two stages. The 2 : 3-dinitro-*p*-toluenesulphonylanisidine (compare Abstr., 1909, 377) when heated at 70° with nitric acid (D 1·4) gives a good yield of *toluene*-p-*sulphonyltrinitroanisidine*, $OMe\cdot C_6H(NO_2)_3\cdot NH\cdot C_7H_7\cdot SO_2$, a colourless compound, m. p. 221°, accompanied by the *o*-nitrotoluenesulphonyl derivative of trinitro-*p*-anisidine (Abstr., 1912, i, 183). Both products are readily hydrolysed by concentrated sulphuric acid.

Better results are obtained from 4-*p*-toluenesulphonylphenetidine, which has given rise to a *dinitro*-product, then a *trinitro*-compound, m. p. 215—219°, and finally *trinitro*-p-*phenetidine*, $OEt\cdot C_6H(NO_2)_3\cdot NH_2$, which behaves similarly to the corresponding anisidine. It crystallises in red needles, m. p. 124—125°, and yields an *acetyl* compound, colourless needles, m. p. 241—245°, and also the following derivatives of 2 : 6-dinitro-*p*-phenetidine : the 3-*methylamino*-, red needles, m. p. 169—170°, by the action of methylamine ; the 3-*anilino*-, m. p. 151°, by the action of aniline ; the 3-*hydroxy*-, m. p. 167°, by the action of sodium acetate, and the 3-*amino*-, red crystals, m. p. 243—246°, by the action of alcoholic ammonia. The latter is not diazotisable, but gives none of the reactions of *o*-diamines.

J. C. W.

Action of Nitric Acid on Halogen Derivatives of *o*-Alkylphenols. THEODOR ZINCKE (*Annalen*, 1912, **394**, 1—3).—The product obtained by the fission of tetrabromo-*o*-methylquinnitrole nitrate by alkalis (Zincke and Klostermann, Abstr., 1907, i, 322) can be converted into a substance, C_9Br_6O, which is apparently perbromoindone. The various stages of the change, however, do not proceed quite satisfactorily, consequently the corresponding chlorinated compounds have been prepared and examined (following abstract). C. S.

Tetrachloro-*o*-cresol and its Conversion into Perchloroindone. THEODOR ZINCKE and W. PFAFFENDORF (*Annalen*, 1912, **394**, 3—22. Compare preceding abstract).—By keeping for ten to twelve hours a solution of 6-chloro-*o*-toluidine in glacial acetic and concentrated hydrochloric acids saturated with chlorine, 3 : 3 : 4 : 5 : 5 : 6-*hexachloro*-2-*keto*-1-*methyl*-Δ^1-cyclo*hexene*,

$$CHCl<\begin{matrix}CCl_2\cdot CO-\\CCl_2\cdot CCl\end{matrix}>CMe,$$

m. p. 107°, is obtained. It crystallises in large, monoclinic prisms, has an odour of camphor, slowly dissolves in alkalis with a yellow colour, liberates iodine from acidified potassium iodide, is scarcely attacked by concentrated sulphuric acid, can be recrystallised from nitric acid (D 1·4), and reacts with sodium acetate in boiling alcohol to form a *pentachloro*-6-*keto*-1-*methyl*cyclo*hexadiene*, $CO<\begin{matrix}CCl_2\cdot CCl\\CMe:CCl\end{matrix}>CCl$ or

$$CO<\begin{matrix}CCl:CCl-\\CMe:CCl\end{matrix}>CCl_2,$$

m. p. 64°, b. p. 165°/15 mm. By reduction with stannous chloride and acetic and hydrochloric acids, the former ketochloride yields a mixture of tri- and tetra-chloro-*o*-cresol, whilst the latter yields only *tetrachloro*-o-*cresol*, $C_7H_4OCl_4$, m. p. 190°, colourless needles (*acetate*, m. p. 136°; *methyl ether*, m. p. 114°).

Tetrachloro-*o*-cresol forms a quinnitrole nitrate even under the conditions under which tetrabromo-*o*-cresol forms the quinnitrole (Abstr., 1907, i, 322). It is obtained best by slowly adding tetrachloro-*o*-cresol to nitric acid (D 1·48) with cooling. *Tetrachloro*-o-*methylquinnitrole nitrate*, $CCl<\begin{matrix}CCl\cdot CMe(NO_2)\\CCl:CCl\text{———}\end{matrix}>C(OH)\cdot O\cdot NO_2$, m. p. 93—94° (decomp.), colourless prisms, is converted into trichloro-*p*-toluquinone above its m. p. or by concentrated sulphuric acid at 100—120°, and by heating with petroleum or formic or acetic acid into *tetrachloro*-o-*methylquinol*, $OH\cdot CMe<\begin{matrix}CO-CCl\\CCl:CCl\end{matrix}>CCl$, m. p. 114—115°, faintly yellow prisms (*acetate*, m. p. 86°, yellow plates; *anilide*, m. p. 172°, yellow leaflets). The quinnitrole nitrate is not directly reconverted into tetrachloro-*o*-cresol by reduction, but yields it by treatment with boiling glacial acetic acid and subsequently with stannous chloride, the quinol being formed as an intermediate product. The quinol is converted into trichloro-*p*-toluquinone by heating with acetic and sulphuric acids, and yields the quinnitrole nitrate by treating its ethereal solution with nitrous fumes.

The quinnitrole nitrate is decomposed by aqueous sodium carbonate

and yields, after acidification of the solution, a substance, $C_7H_4O_6N_2Cl_4$, m. p. 142° (decomp.), colourless needles, to which is ascribed the formula $NO_2 \cdot CHMe \cdot CCl:CCl \cdot CCl:CCl \cdot CO_2 \cdot NO_2$, analogous to that of the corresponding brominated compound (*loc. cit.*). The substance has not been converted into tetrachloro-*o*-cresol, but yields trichloro-*p*-toluquinone by heating with acetic anhydride. It is converted by concentrated sulphuric acid at 105° into the substance, $C_{10}O_2Cl_8$, m. p. 164—170°, obtained by the action of acetic acid and sodium acetate on pentachloro*cyclo*pentenone (Zincke and Meyer, Abstr., 1909, i, 591). The substance $C_{10}O_2Cl_8$ forms a *methyl alcoholate*, m. p. 138°, yellow plates, and an *ethyl alcoholate*, m. p. 99°, of hexachloroindone (possibly $C_6Cl_4<\genfrac{}{}{0pt}{}{\overline{\quad\quad\quad CCl}}{C(OH)(OR)}>CCl$) by boiling with methyl or ethyl alcohol, and yields above its m. p. a *substance*, C_9OCl_8, m. p. 123—124°, colourless needles, which has the formula $CCl<\genfrac{}{}{0pt}{}{CO-CCl \cdot CCl:CCl}{CCl \cdot CCl \cdot CCl:CCl}$; this substance is converted into hexachloroindone by heating with acetic acid and sodium acetate or by stannous chloride, and yields octachlorohydrindone when carefully heated over a free flame. C. S.

Rearrangement of Allyl Ethers of Phenols into *C*-Allylphenols. LUDWIG CLAISEN [and O. EISLEB] (*Ber.*, 1912, 45, 3157—3166).—Whereas *O*-alkyl derivatives of ethyl acetoacetate or of hydroxymethylene compounds can usually be distilled unchanged, the *O*-allyl derivatives readily pass over into *C*-allyl derivatives. The transformation has been investigated in the case of certain phenols and phenolcarboxylic acids.

β-Naphthyl allyl ether, $C_{10}H_7 \cdot O \cdot C_3H_5$, before distillation is a colourless, sweet smelling oil, insoluble in sodium hydroxide, and giving no coloration with ferric chloride. When distilled, it undergoes partial conversion into the isomeric 1-*allyl-β-naphthol*, $C_3H_5 \cdot C_{10}H_6 \cdot OH$; complete conversion is effected by heating at 210°. The oil, which is faintly yellow-coloured, distils at 177—178°/12 mm., and crystallises in well-formed colourless prisms, m. p. 55°. It gives a green coloration with ferric chloride. The *benzoate* separates in colourless crystals, m. p. 65°.

1-*Allyl-β-naphthyl allyl ether* is a colourless oil of faint odour, b. p. 178°/13 mm. The second allyl group could not be made to wander to the nucleus.

Guaiacyl allyl ether, $OMe \cdot C_6H_4 \cdot O \cdot C_3H_5$, is a colourless liquid of very little odour, b. p. 116°/14 mm., D^{15} 1·058. When heated at 230°, it is converted into C-*allylguaiacol*, $OMe \cdot C_6H_3(C_3H_5) \cdot OH$, a colourless oil with an odour of pinks, b. p. 122°/12 mm., D^{15} 1·071°. The *sodium* salt forms colourless needles; the *phenylurethane* crystallises in colourless needles, m. p. 101°; the p-*nitrobenzoate* forms short, flat prisms, m. p. 97°. Although allylguaiacol is very similar to eugenol, the two phenols are probably not identical. *Eugenyl* p-*nitrobenzoate* crystallises in long, faintly yellow needles, m. p. 81°.

Evidence that the above changes do not involve rearrangement of the allyl group, $CH_2:CH \cdot CH_2$, into propenyl, $CH_3 \cdot CH:CH$, is

afforded in the case of ethyl *o*-allyloxybenzoate, $C_3H_5 \cdot O \cdot C_6H_4 \cdot CO_2Et$ which is converted on distillation into ethyl *C*-allylsalicylate,

$$C_3H_5 \cdot C_6H_3(OH) \cdot CO_2Et.$$

On hydrolysis with methyl alcoholic potassium hydroxide, *C*-allylsalicylic acid, $CH_2{:}CH \cdot CH_2 \cdot C_6H_3(OH) \cdot CO_2H$, is obtained; when this is heated at 170° with potassium hydroxide and a little water, it undergoes rearrangement into *C*-propenylsalicylic acid,

$$CHMe{:}CH \cdot C_6H_3(OH) \cdot CO_2H.$$

Scichilone (Abstr., 1883, 335), who observed the conversion of methyl *o*-allyloxybenzoate into allylsalicylic acid, m. p. 113°, obtained in reality a mixture of the *C*-allyl- and *C*-propenyl-salicylic acids.

Ethyl *o*-allyloxybenzoate is an oil, b. p. 153°/13 mm., giving no coloration with ferric chloride. On hydrolysis with methyl alcoholic potassium hydroxide, *o*-allyloxybenzoic acid is obtained in colourless platelets, m. p. 65°.

Ethyl *C*-allylsalicylate is an oil, b. p. 142°/12 mm.; it gives a deep bluish-violet coloration with ferric chloride. *C*-Allylsalicylic acid crystallises in colourless needles, m. p. 96°. *C*-Propenylsalicylic acid crystallises in long, colourless needles, m. p. 158°, giving an indigo-blue coloration with ferric chloride. E. F. A.

Physico-chemical Studies of Photographic Developers. I. Quinol–Sulphite Developer. NIKOLAI SCHILOFF and S. FEDOTOFF (*Zeitsch. Elektrochem.*, 1912, 18, 929—939).—The nature of the changes accompanying the absorption of oxygen by quinol solutions containing sodium sulphite has been investigated.

In presence of sodium sulphite, not only is a larger quantity of oxygen absorbed by a given quinol solution, but the reaction is unaccompanied by the formation of brown resinous products, and its velocity, although smaller, falls off much less rapidly. In the early stages of the reaction, the oxidation of the quinol induces simultaneous oxidation of the sulphite, but this coupled action soon ceases, as is shown by the data obtained in the estimation of the sulphite and sulphate at successive stages of the reaction. These show that the oxygen absorbed in the later stages of the reaction is unaccompanied by any appreciable alteration of the concentration of sulphite and sulphate. The molecular ratio of the sulphite, which disappears without giving rise to sulphate, to oxidised quinol is as 2 : 1.

Unless the sulphite is present in the quinol solution at the beginning of the reaction, it has no appreciable influence on the course of the change, oxidation and decomposition products of quinol being formed which are incapable of reacting with the sulphite.

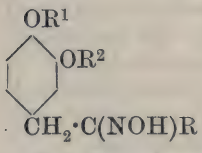
The series of colour changes which occur during the progress of the reaction and the changes in the reaction velocity both indicate the formation of three intermediate products which probably all contain sodium sulphite.

On the assumption that the primary oxidation of quinol gives rise to peroxides, evidence of which has been obtained by Sheppard and Mees, the observed facts lead to the view that the following changes are involved: (1) quinol + O_2 $\longrightarrow$ peroxide; (2) peroxide + sodium sulphite $\longrightarrow$ sodium sulphate + intermediate substance *A*; (3) inter-

mediate substance A + sodium sulphite → additive compound A (A + sulphite); (4) additive compound $A + O_2$ → additive compound $B + O_2$ → additive compound C. These additive compounds all contain two molecules of sodium sulphite per molecule of oxidised quinol. The sulphite present in these additive compounds does not react with iodine in neutral or slightly acid solution.

In the absence of sulphite, the absorption of oxygen by quinol solutions involves the changes: (1) quinol $+ O_2$ → peroxide; (2) peroxide + quinol → unstable intermediate substance $+ O_2$ → resinous products. H. M. D.

Preparation of 3 : 4-Dihydroxyphenylalkylamines. KARL W. ROSENMUND, CARL MANNICH, and WILLY JACOBSOHN (D.R.-P. 247906. Compare this vol., i, 443).—Dihydroxyphenylalkylamines can be readily prepared by reducing oximes of the annexed general formula (where R^1 and R^2 are alkyl groups, and R alkyl or hydrogen), and subsequently converting the alkyloxy- into a hydroxy-group.



3 : 4-*Dimethoxybenzyl methyl ketone*, $C_6H_3(OMe)_2\cdot CH_2\cdot COMe$, a colourless oil, b. p. 198°/20 mm. (prepared from *iso*eugenyl methyl ether), is converted into its *oxime*; this when reduced with sodium amalgam in acetic acid solution furnishes 3 : 4-*dimethoxyphenyl*iso*propylamine*, b. p. 166—168°/20 mm. (the *hydrochloride* has m. p. 148°), which on hydrolysis by boiling with colourless hydriodic acid (D 1·69) yields 3 : 4-*dihydroxyphenyl*iso*propylamine hydriodide*, a syrup which subsequently becomes crystalline, and is converted into the *hydrochloride* (m. p. 190—192°) of the *base*,

$$C_6H_3(OH)_2\cdot CH_2\cdot CHMe\cdot NH_2.$$

3 : 4-*Dihydroxyphenylethylamine*, $C_6H_3(OH)_2\cdot CH_2\cdot CH_2\cdot NH_2$, is isolated in the form of its *hydrochloride*, m. p. 174—175°, and obtained by the reduction of homoveratraldehydeoxime (which was not isolated) to 3 : 4-*dimethoxyphenylethylamine*, an oil, b. p. 188°/15 mm.; the *hydrochloride*, a syrup, difficult to crystallise; in this case the hydrolysis of the methoxy-groups is carried out with concentrated hydrochloric acid (4 parts) at 150° during two hours. F. M. G. M.

Preparation of Di- and Poly-hydroxybenzene Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249939. Compare Abstr., 1885, 145; 1906, i, 559).—When substituted phenols are heated with alkaline earth oxides or hydroxides (the presence of iodine is optional), the substituted group is converted into hydroxyl. Catechol (b. p. 240—245°) is thus obtained when *o*-chlorophenol (130 parts) is heated during nine hours at 170° with crystalline strontium hydroxide (530 parts) and 500 parts of water, whilst *p*-chlorophenol under similar treatment furnishes quinol.

F. M. G. M.

Aromatic Sulphine Bases. III. FRIEDRICH KEHRMANN and GEORGES A. SAVA (*Ber.*, 1912, **45**, 2895—2901. Compare Abstr., 1906, i, 83, 949; Smiles, Trans., 1906, **86**, 696).—The paper contains

a description of the following compounds. Lead *p*-tolyl mercaptide and methyl sulphate (5 mols.) at 100° for one and a-half hours yield the *methosulphate* of *p*-tolyldimethylsulphine hydroxide,

$$C_7H_7\cdot SMe_2\cdot O\cdot SO_3Me;$$

the *mercurichloride*, $C_9H_{13}SCl,HgCl_2$, m. p. 118—120°, colourless needles, *platinichloride*, *picrate*, *perchlorate*, *iodide*, and *dichromate* are described. An aqueous solution of the *base* has a caustic taste and alkaline reaction, liberates ammonia from ammonium salts, and absorbs carbon dioxide; by concentration it yields *p*-tolyl methyl sulphide. *β-Naphthyldimethylsulphine mercurichloride*, m. p. 114—116° (decomp.), *platinichloride*, *perchlorate*, m. p. 151—153°, and *chloride* are described; the last easily decomposes into methyl chloride and *β*-naphthyl methyl sulphide, which is also obtained by boiling an aqueous solution of the *base*. The *methosulphate*, *mercurichloride*, and *platinichloride* of *β*-anthryldimethylsulphine hydroxide are mentioned. *o*-Anisyldimethylsulphine hydroxide forms a *mercurichloride*, m. p. 121—122°, *platinichloride*, *iodide*, and *chloride*. *p*-Anisyldimethylsulphine hydroxide forms a *mercurichloride*, m. p. 121—122°, and *platinichloride*, and the meta-isomeride yields a *mercurichloride*, m. p. 134—135° (decomp.), *platinichloride*, *picrate*, m. p. 130—132°, *dichromate*, m. p. 67—70°, *perchlorate*, m. p. 122°, *chloride*, *bromide*, and *iodide*, m. p. about 122° (decomp.). The *mercurichloride*, m. p. 142—143° (decomp.), *platinichloride*, *iodide*, m. p. 91°, *perchlorate*, m. p. 140—141°, *picrate*, m. p. 140—141°, *ferricyanide*, m. p. 116° (decomp.), and *dichromate* of *o*-phenetyldimethylsulphine hydroxide, and the *mercurichloride*, m. p. 111—112°, and *platinichloride* of the para-compound are described. C. S.

Syntheses in the Fatty-aromatic Series. VIII. Tertiary Derivatives of *o*- and *p*-Aminobenzyl Alcohol. JULIUS VON BRAUN and O. KRUBER (*Ber.*, 1912, 45, 2977—2997).—*p*-Aminobenzylaniline and its derivatives undergo an interesting condensation with aromatic amines with the formation of diphenylmethane derivatives (compare Cohn and Fischer, Abstr., 1900, i, 690). In order to throw light on the method of this condensation, dialkylaminobenzyl alcohols have been prepared by the action of formaldehyde on tertiary amines; the products are yellow, distillable liquids, which exhibit the ordinary reactions for the hydroxyl and tertiary amino-groups, but they condense much less readily than the primary and secondary aminobenzyl alcohols with other aromatic molecules; it is therefore suggested that the easy formation of anhydrides by the primary and secondary amino-compounds is connected with the greater relative reactivity of these substances, the process being really not one of condensation, but an addition of the second molecule to the anhydride molecule. The earlier suggestion (von Braun, Abstr., 1908, i, 684) that the above diphenylmethane derivative formation is due to primary hydrolytic scission of the aminobenzylaniline compound to an aminobenzyl alcohol, which then condenses with the aromatic amine, is relinquished.

Dimethyl-*p*-toluidine when heated for twenty-four hours on the water-bath with an equal weight of concentrated hydrochloric acid and three times the weight of 40% formaldehyde solution undergoes

condensation with the formation of 2-*dimethylamino-5-methylbenzyl alcohol*, a yellow oil of feeble odour, b. p. 250°, with slight decomposition, m. p. 30°; *hydrochloride*, oily; *platinichloride*, red crystals, m. p. 182° (decomp.); *picrate*, yellow leaflets, m. p. 160°; *methiodide*, colourless tablets, m. p. 147° (decomp.). The free amino-alcohol on treatment with concentrated hydrochloric acid in a tube at 100°, or with phosphorus pentachloride in light petroleum solution, gives the *hydrochloride* of 6-*dimethylamino-3-methylbenzyl chloride*, from which the yellowish-red *platinichloride*, m. p. 195°, can be obtained; the chlorine in the side-chain of the molecule is, however, so loosely attached that it is removed by water and by alkali with the formation of a mixture of the original alcoholic base and 6-*dimethylamino*-3-*methylbenzyl ether*, $(NMe_2{\cdot}C_6H_3Me{\cdot}CH_2)_2O$, which is more conveniently prepared by the dehydration of the amino-alcohol with twice its weight of strong sulphuric acid on the water-bath; it is an inodorous, colourless, viscous oil, b. p. 222—224°/19 mm.; *picrate*, m. p. 175°; *methiodide*, m. p. 186°; the ether base can be slowly but completely hydrolysed to the original alcohol base by boiling with dilute sulphuric acid.

Unlike 6-dimethylamino-3-methylbenzyl chloride, the esters with organic acids are stable substances. The *acetate*, colourless liquid, b. p. 144—145°/16 mm., gives a *picrate*, yellow needles, m. p. 117°, a yellowish-red *platinichloride*, m. p. 169°, and an oily *methiodide*. The *benzoate* is a viscid oil, b. p. 226—228°/16 mm. (slight decomp.); *picrate*, m. p. 137—138°. The m-*nitrobenzoate* is a colourless, crystalline solid, m. p. 64°; *picrate*, m. p. 154°.

In the preparation of 6-dimethylamino-3-methylbenzyl alcohol, a too extended heating of the reaction mixture causes partial oxidation to 4-*dimethylamino-3-toluic acid*, $NMe_2{\cdot}C_6H_3Me{\cdot}CO_2H$, which is also obtainable by direct oxidation of the amino-alcohol with chromic acid; the *hydrochloride*, m. p. 188—189° (decomp.), can be converted into the yellow *platinichloride*, m. p. 217—218°. Towards reducing agents, dimethylaminomethylbenzyl alcohol is remarkably resistant, but it is reduced by sodium and alcohol to as-*dimethyl*-m-*xylidine*, $C_6H_3Me_2{\cdot}NMe_2$, b. p. 205°; *picrate*, m. p. 123—124°; *platinichloride*, m. p. 219°. The same reduction product was obtained in an endeavour to dehydrate the dimethylaminobenzyl alcohol molecule to an indole ring (compare Paal and Laudenheimer, Abstr., 1893, i, 37) by heating with zinc chloride; 1 : 5-*dimethylindole*, prepared from p-tolylmethylnitrosoamine (compare Hegel, Abstr., 1886, 552) for comparison, has b. p. 138°/17 mm., 262°/753 mm., D_4^{20} 1·0242, and on reduction with zinc and hydrochloric acid yields the 2 : 3-*dihydro*-derivative, falsely expected from the dehydration of the alcoholic base, b. p. 119—120°/18 mm., 233—234°/755 mm., D_4^{20} 0·9811; *platinichloride*, m. p. 203—204°; *picrate*, m. p. 177°.

Dimethylaminomethylbenzyl alcohol shows but little tendency to condense with other aromatic molecules. With methylaniline it gives a condensation *product*, boiling above 200° in a vacuum. When heated on the water-bath with excess of aniline in 15% hydrochloric acid for twenty-four hours, it gives a small yield of 4′-*aminophenyl*-6-*dimethylamino*-m-*tolylmethane*, $NMe_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}C_6H_4{\cdot}NH_2$, a viscid

liquid, b. p. 220—224°/17 mm. If zinc chloride is used as the condensation agent, the amino-alcohol will condense with tertiary amines; thus, with dimethylaniline at 180°, it then gives colourless 4 : 6′-*tetramethyldiaminophenyl*-m-*tolylmethane*,

$$NMe_2\cdot C_6H_3Me\cdot CH_2\cdot C_6H_4\cdot NMe_2,$$

m. p. 83—84°, b. p. 250—252°/16 mm.; *hydrochloride*, m. p. 203°; *picrate*, reddish-yellow leaflets, m. p. 180—182°; yellow *platinichloride*, m. p. 197° (decomp.); *methiodide*, m. p. 204°. In an analogous manner, dimethyl-*p*-toluidine gives a very viscous, yellow oil, 2 : 2′-tetramethyldiamino-5 : 5′-di-*m*-tolylmethane, $CH_2(C_6H_3Me\cdot NMe)_2$, b. p. 212—214°/16 mm. (compare von Braun, *loc. cit.*).

Dimethyl-*o*-toluidine is already known to show considerable resistance towards condensation with aldehydes (Weinberg, Abstr., 1892, 1078; Alexander, *ibid.*, 1320); however, by using a large excess of formaldehyde and extending the time for reaction, 4-*dimethylamino*-3-*methylbenzyl alcohol* can be obtained by a similar process to that for the isomeric 2-dimethylamino-5-methylbenzyl alcohol above; it is a yellow liquid, b. p. 147°/11 mm., giving an oily *hydrochloride*, *picrate*, m. p. 119°, a syrupy *methiodide*, colourless *acetate*, b. p. 156—158°/16 mm. (*picrate*, m. p. 133°), m-*nitrobenzoate*, m. p. 64° (*picrate*, m. p. 120°). This alcoholic base shows great resistance to sodium and alcohol, and only a few drops of the *as*-dimethyl-*m*-xylidine could be obtained; it also condenses with difficulty with dimethylaniline in the presence of zinc chloride, giving a poor yield of 4 : 4′-*tetramethyldiaminophenyl*-*m*-*tolylmethane*, $NMe_2\cdot C_6H_3Me\cdot CH_2\cdot C_6H_4\cdot NMe_2$, a colourless, viscous oil, b. p. 247—249°/17 mm.; *platinichloride*, unstable; *picrate*, m. p. 183°.

4-*Dimethylaminobenzyl alcohol* is obtained in very small amount from the reaction product by treating dimethylaniline with an equal weight of concentrated hydrochloric acid and twice its weight of 40% formaldehyde solution for eight hours on the water-bath. The properties of the product do not agree with those stated by Rousset (Abstr., 1895, i, 176). It is a yellow oil with an odour more pleasant than that of dimethylaniline; *platinichloride*, m. p. 181°; *picrate*, yellow needles, m. p. 130°; *methiodide*, m. p. 126°; the *acetate*, b. p. 142—144°/18 mm., gives a badly crystalline *platinichloride*, and a *picrate*, m. p. 113—114°; the *benzoate* is a viscous oil, b. p. 216—218°/16 mm., which gives an amorphous *platinichloride*, m. p. 179—180°, and a *picrate*, yellow needles, m. p. 117°; the m-*nitrobenzoate* is colourless, m. p. 51°, and gives a *picrate*, m. p. 146°. 4-*Dimethylaminobenzyl chloride* was produced by the action of hydrochloric acid on the amino-alcohol, as an unstable substance which could be isolated as the yellow *platinichloride*, m. p. 187°. The amino-alcohol condenses easily with dimethylaniline in the presence of zinc chloride, with the formation of *s*-tetramethyldiaminodiphenylmethane.

The condensation of formaldehyde with 1-phenylpiperidine yields some p-*piperidylbenzyl alcohol*, a yellow oil, b. p. 172—176°/12 mm.; *platinichloride*, m. p. 190°. The amino-alcohol condenses with phenylpiperidine in the presence of zinc chloride, giving *dipiperidyldiphenylmethane*, m. p. 84° (*platinichloride*, decomposes at 235°; *methiodide*, m. p. 217° with decomp.; *dibenzoyl* derivative, m. p. 250°), which

also accompanies the amino-alcohol in its original formation, but which is more satisfactorily obtained by treating an alcoholic solution of *p*-diaminodiphenylmethane with dibromopentane (compare von Braun, *loc. cit.*; also Abstr., 1904, i, 841).

Diethylaminobenzyl alcohol, obtained from the condensation of formaldehyde and diethylaniline in hydrochloric acid solution, is surprisingly unstable; it is a yellow liquid, b. p. 165°/9 mm.; *picrate*, m. p. 101°; *methiodide*, m. p. 149°; *acetate*, colourless oil, b. p. 178—180°/17 mm. It is easily decomposed by dilute acids with the formation of s-*tetraethyldiaminodiphenylmethane*, m. p. 41° (*picrate*, m. p. 191°), which therefore accompanies the amino-alcohol in its preparation. On account of its instability, the behaviour of diethylaminobenzyl alcohol towards reduction and condensation with aromatic amines could not be investigated. It is, however, oxidisable to the already known *p*-diethylaminobenzoic acid.

It was found impossible to produce sufficient condensation of formaldehyde with diethyl-*o*- or -*p*-toluidine to obtain appreciable quantities of the corresponding aminobenzyl alcohols. D. F. T.

Oxonium Compounds. II. George L. Stadnikoff (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1219—1247).—In order to confirm his views concerning the mechanism of the Grignard reaction (compare this vol., i, 109), the author has carried out a number of further experiments under conditions excluding the possibility of isomeric change.

The formation of tetraphenylethane on distillation in a vacuum of the product obtained by the action of diphenylmethyl butyl ether on magnesium propyl iodide in the cold shows that the structure of monoetherates of organo-magnesium compounds is expressed by Grignard's formula, $RR{:}OR{\cdot}MgI$, and not by that of Baeyer, $RR{:}OI{\cdot}MgR$. The action of alkyl haloid on this compound being expressed by the equation: $RR{:}OR{\cdot}MgI + R'I = MgI_2 + R_2O + R{\cdot}R'$, the author regards it as most probable that the first stage of this reaction results in the formation of a tetra-alkyloxonium compound: $RR'{:}O{:}RR''$. With water the decomposition should give rise to an unstable trialkyloxonium compound, $RR'{:}O{:}R''H$, which would decompose with formation of $R{\cdot}H$ and $R{\cdot}R'$; experiment shows that this actually occurs. For instance, in the decomposition by water of the compound $\begin{matrix}C_4H_9\\CHPh_2\end{matrix}{>}O{<}\begin{matrix}Pr\\MgI\end{matrix}$, 12·5% of the latter gives propane, 14·5% tetraphenylethane, and 38·5% diphenylbutane

The results of further experiments made to determine the relation of the amount of ether taking part in the reaction to that of the organo-magnesium compound (compare Bredig, *Zeitsch. Elektrochem.*, 1903, 9, 753) are in contradiction to Tschelinzeff's statement that ether plays the part of a catalyst in Grignard's reaction ("Organo-magnesium Compounds," Moscow, 1908, 54). T. H. P.

Action of Carbon Dioxide on Etherates of Magnesium Alkyl Haloids. George L. Stadnikoff and (Mme.) Z. A. Kuzmina-Aron (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1247—1256).—The etherates

formed from ethers and organo-magnesium compounds, when dissolved in benzene or xylene, do not react with carbon dioxide, and the authors have now investigated this action in ethyl ethereal solution. Two possibilities present themselves: (1) According to Tschelinzeff's views ("Organo-magnesium Compounds," Moscow, 1908, 177) and on the assumption that the structure attributed by Stadnikoff (compare preceding abstract) to these etherates is correct, the ethyl ether should displace a molecule of an ether and this displacement should proceed in various ways; thus, $C_4H_9\cdot OPr(CHPh_2)\cdot MgI + Et_2O$ should give (*a*) $CHPh_2\cdot O\cdot C_4H_9 + OEt_2Pr\cdot MgI$,

(*b*) $CHPh_2\cdot OPr + C_4H_9\cdot OEt_2\cdot MgI$,

and (*c*) $C_4H_9\cdot OPr + CHPh_2\cdot OEt_2\cdot MgI$. (2) The etherate may merely dissolve in the ethyl ether. In this case the action of carbon dioxide should yield $C_4H_9\cdot OPr(CHPh_2)\cdot CO_2MgI$, which would be converted by dilute sulphuric acid into the compound, $C_4H_9\cdot OPr(CHPh_2)\cdot CO_2H$. The latter, being unstable, would undergo decomposition, for which three methods are possible: (*a*) $CHPh_2\cdot O\cdot C_4H_9 + Pr\cdot CO_2H$; (*b*) $CHPh_2\cdot OPr + C_4H_9\cdot CO_2H$, and (*c*) $C_4H_9\cdot OPr + CHPh_2\cdot CO_2H$.

The experiments as yet made do not indicate the formation of organic acids in this decomposition, which yields carbon dioxide, propane, butane, ethers, tetraphenylethane, *αα*-diphenylbutane, etc. As product of the action of carbon dioxide, an oily compound has been obtained, this being apparently of the composition

$(CHPh_2)(C_4H_9)\dot{:}OPr\cdot CO_2MgI,Et_2O$;

the ether is given up in a vacuum. T. H. P.

Reply to Gorsky's "Mechanism of the Grignard Reaction." GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1256—1264).—Polemical against Gorsky (this vol., i, 622).

T. H. P.

Action of Formic Acid on Triarylcarbinols. ALFRED GUYOT and A. KOVACHE (*Compt. rend.*, 1912, **155**, 838—840. Compare this vol., i, 186; and Kauffmann and Pannwitz, this vol., i, 351).—Crystallisable formic acid, whilst reducing triarylcarbinols, does not have this effect on other molecules containing reducible groups, the reaction being specific for this one class of compounds. A study of the reaction in the case of a large number of such carbinols shows that the reaction is not always quantitative. If, however, a certain quantity of anhydrous sodium formate is previously added to the formic acid, the transformation of the carbinol into hydrocarbon and the evolution of carbon dioxide are theoretical, thus giving a method for the quantitative estimation of such compounds. The part played by the sodium formate is apparently to prevent any dehydrating action of the formic acid. W. G.

Betulin. II. I. K. TRAUBENBERG (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1202—1208).—More energetic oxidation of betulin by means of chromic acid than that previously employed (this vol., i, 260) yields betulinic acid and the ketone, $C_{24}H_{38}O_2$, but no diketone,

so that betulin contains only one hydroxyl group of secondary character.

The betulinic acid obtained in the above manner, and regarded by Hausmann (Abstr., 1877, i, 94) as possessing the composition $C_{36}H_{54}O_6$, appears to be, not an individual product, but a mixture of an acid, $C_{12}H_{20}O$, and a hydrocarbon, $C_{12}H_{18}$, the dry distillation of betulin proceeding according to the equation: $C_{24}H_{40}O_2 = H_2O + C_{12}H_{20}O + C_{12}H_{18}$.

Oxidation of the betulin by means of fuming nitric acid yields a dinitro-acid, $C_{22}H_{32}O_{10}N_2$, m. p. 203—205°. Analysis of the compound obtained by treating this acid with phenylhydrazine gives indefinite results, explainable as due to the formation either of a dihydrazone or of a monohydrazone in which the two nitro-groups are reduced to amino-groups. T. H. P.

Crystalline Form of Δ¹-cycloHexene-1-α-isobutyric Acid. PETR N. TSCHIRWINSKY (*Zeitsch. Kryst. Min.*, 1912, **51**, 303; from *Schriften Ural Ges. Naturf.*, 1909, **29**, 113—117).—Crystals of the acid, $C_6H_9\cdot CMe_2\cdot CO_2H$, prepared by O. Wallach (Abstr., 1908, i, 406) are orthorhombic, with $a:b:c = 0\cdot914:1:0\cdot359$. L. J. S.

New Aromatic Ethereal Salts Formed by the Interaction of o-Sulphobenzoic Anhydride and Phenols in the Presence of Water and an Alkali Hydroxide. ARNOLD H. C. HEITMAN (*J. Amer. Chem. Soc.*, 1912, **34**, 1591—1597).—The following method has been found to yield alkali salts of esters of the general formula, $SO_3X\cdot C_6H_4\cdot CO_2R$. *o*-Sulphobenzoic anhydride (1 mol.) is suspended in about 5 parts of water at 0°, and treated with alkali hydroxide (1 mol.) and a phenol (1 mol.) also dissolved in the same quantity of water at 0°. The mixture is shaken until solution results and is then filtered. The phenol, remaining in the solution, is extracted with ether, the aqueous solution concentrated to about one-fifth of the original volume and allowed to crystallise. The salts are soluble in water or alcohol, stable in the air or in solution, and are readily hydrolysed by warm dilute solutions of alkali carbonates with formation of the phenol and alkali *o*-sulphobenzoate. It is suggested that they may prove of value for the synthesis of physiologically active substances.

The following salts are described: *Potassium phenyl* o-*sulphobenzoate*, $SO_3K\cdot C_6H_4\cdot CO_2Ph$, m. p. 277—280°. *Barium phenyl* o-*sulphobenzoate*. *Potassium ethyl* o-*sulphobenzoyloxybenzoate*,

$$SO_3K\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2Et,$$

m. p. 246°, from ethyl salicylate. *Barium guaiacyl* o-*sulphobenzoate*, $Ba(SO_3\cdot C_6H_4\cdot CO\cdot OC_6H_4\cdot OMe)_2$. *Sodium thymyl* o-*sulphobenzoate*, $SO_3Na\cdot C_6H_4\cdot CO\cdot OC_6H_3Me\cdot CHMe_2$. *Sodium phenolphthalein* o-*sulphobenzoate*. All these salts are crystalline, with the exception of the last two which are obtained as amorphous powders. E. G.

Preparation of Esters of Glycols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 248255).—The following acids can be employed for the preparation of glycyl esters: phenylacetic, α-phenyl-

propionic, α-phenylbutyric, α-phenyl-α-ethylbutyric, and β-phenylpropionic acids.

Phenyldiethylcarbinylacetic [*α-Phenyl-β-ethylvaleric*] *acid*,

$$CHEt_2\cdot CHPh\cdot CO_2H,$$

is prepared by the interaction of sodium phenylacetonitrile and diethylcarbinyl bromide and subsequent hydrolysis.

Glycyl phenylacetate, b. p. 185—190°/25 mm., is obtained from ethylene glycol and phenylacetic acid, whilst the *ester* from ethylene dichloride and α-phenylbutyric acid has b. p. 166°/4 mm.

Glycyl β-phenylpropionate has b. p. 180°/16 mm. F. M. G. M.

Preparation of Acids containing an Aryl Group in the α-Position. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 248777).—The amides and carbamides of α-aryl acids of general formula $CRR^1R^2\cdot CO_2H$ (where R is aryl, and R^1 and R^2 alkyl groups) are of therapeutic value, and the following are now described:

α-Phenyl-α-propylvaleronitrile, $CPhPr_2\cdot CN$, b. p. 157—159°/30 mm. (prepared from phenylacetonitrile), when heated with alcoholic potassium hydroxide during seven hours at 120—130°, furnishes *α-phenyl-α-propylvaleramide*, prisms, m. p. 91—92°, whilst *α-phenyl-α-ethylbutyronitrile*, $CPhEt_2\cdot CN$, an oil, b. p. 139°/22 mm., yields *α-phenyl-α-ethylbutyramide*, m. p. 53°.

α-Phenyl-α-ethylbutyrylcarbamide, prepared from carbamide and α-phenyl-α-ethylbutyryl chloride, has m. p. 132—133°. F. M. G. M.

Preparation of Derivatives of α-Aryl Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249241. Compare Abstr., 1889, 861, and preceding abstract).—The amides and carbamides of α-aryl acids of general formula $R^1CHR\cdot CO_2H$ (where R^1 is aryl, and R an alkyl group) are quite tasteless, of therapeutic value, and readily prepared by ordinary methods.

α-Phenyl-*n*-valeric acid, b. p. 280° (*loc. cit.*), furnishes a *chloride*, which yields the corresponding *amide*, m. p. 83—85°, *carbamide*, *glycide*, and *ethylamide*.

α-Phenyl-*n*-butyric acid (phenylethylacetic acid) likewise furnishes a *chloride*, *carbamide*, m. p. 147°, and *amide*, m. p. 86°.

Phenylacetonitrile when treated with sodamide and diethylcarbinol yields *phenyl*iso*amylacetonitrile*; this furnishes the corresponding *acid*, acid *chloride*, and finally *phenyl*iso*amylacetamide*, m. p. 138°.

F. M. G. M.

Determination of the Configuration of the Stereoisomeric Cinnamic Acids. RICHARD STOERMER and PAUL HEYMANN (*Ber.*, 1912, **45**, 3099—3104).—Fischer (compare this vol., i, 187) has recently called attention to the fact that no definite conclusions can be drawn, regarding the configuration of the cinnamic acids, from the reduction of phenylpropiolic acid, since under different conditions both the ordinary and the *allo*- or *iso*-acid may be produced (compare Paal and Hartmann, Abstr., 1909, i, 927). Although the ordinary acid is generally regarded as the *trans*-form, and the *allo*- or *iso*-acid as the *cis*-form, no experimental proof of these configurations has yet been

brought forward. This uncertainty with respect to the configuration of the acids has now been removed, and the correctness of the usual view demonstrated, in the following manner :

Ordinary *o*-nitrocinnamic acid, on exposure to ultra-violet light in pyridine solution, is transformed into a labile isomeride, *allo-o*-nitrocinnamic acid. Both isomerides may be reduced to the corresponding amino-acids, of which the one obtained from the *allo*-acid is at once transformed into carbostyril by passing carbon dioxide through an aqueous solution of its barium salt, and therefore must possess the *cis*-configuration ; on the other hand, the *o*-aminocinnamic acid described by Baeyer and Jackson, and formed by the reduction of the ordinary *o*-nitro-acid, can be converted into carbostyril only by indirect methods, and, therefore, has the *trans*-configuration. On diazotisation and reduction, *trans-o*-aminocinnamic acid yields ordinary cinnamic acid, whereas the *cis*-amino-acid gives rise to *allo*-(or *iso*-)cinnamic acid, which, consequently, must have the *cis*-configuration.

The configuration of the isomeric *o*-amino-acids has also been established by diazotisation and boiling the resulting diazonium compound with water. The amino-acid obtained from *allo-o*-nitrocinnamic acid is directly converted into coumarin, whilst Baeyer and Jackson's *o*-amino-acid yields coumaric acid, which can be converted into the anhydride only by indirect methods.

allo-o-*Nitrocinnamic acid* forms stout, yellowish-white crystals, m. p. 143°, dissolves in concentrated sulphuric acid with a blue coloration, and is much more readily soluble in organic solvents than the *trans*-isomeride, into which it may be converted by exposure to sunlight in chloroform solution containing a trace of bromine. Its solubility in benzene at 18° = 0·69% (*trans*-acid = 0·03%). When dissolved in dilute aqueous ammonia and the solution boiled with ferrous sulphate and excess of barium hydroxide, it yields cis-o-*amino-cinnamic acid*, which, however, could not be isolated in the free condition, but is converted by passing carbon dioxide through the aqueous solution of its barium salt into carbostyril. The diazotisation of the *cis-o*-amino-acid was accomplished by dissolving the theoretical amount of sodium nitrite in the aqueous solution of its barium salt and adding the mixture slowly to cold dilute sulphuric acid. Reduction of the resulting diazonium compound with hypophosphorous acid yielded *iso*cinnamic acid, which was further identified by its conversion into the aniline salt of *allo*-cinnamic acid. The transformation of *trans-o*-aminocinnamic acid into ordinary cinnamic acid was effected in a similar manner. F. B.

Sodium Phenyl Carbonate as Intermediate Product in Kolbe's Synthesis of Salicylic Acid. CARL H. SLUITER (*Ber.*, 1912, 45, 3008—3110. Compare this vol., i, 189).—A reply to Tymstra (this vol., i, 859). Sodium salicylate when heated in a sealed tube for three hours at 250°, and then afterwards kept sealed in the cold for eighteen hours, is found to be unaltered ; the carbon dioxide formed in the dissociation of the salicylate evidently undergoes complete re-absorption. If the heating is carried to 290°, there is some charring, and a little free carbon dioxide is formed, whilst the solid

residue contains some sodium hydrogen carbonate. It is suggested that in this case the sodium phenoxide formed from the dissociation of the salicylate undergoes partial decomposition: $C_6H_5{\cdot}ONa = CH_4 + 4C + CO_2 + NaOH$. These results are held to favour the author's view of the formation of sodium salicylate. D. F. T.

Terephthalaldehyde and Terephthalaldehydic Acid. RUDOLF WEGSCHEIDER and HERMANN SUIDA (*Monatsh.*, 1912, 33, 999—1028).—In an investigation as to the possible occurrence of tautomerism with *p*-aldehydic acids analogous to that exhibited by the ortho-isomerides (Wegscheider, Abstr., 1903, i, 562), the authors have obtained only negative results.

Terephthalaldehyde is obtained more satisfactorily by the simultaneous hydrolysis and oxidation of *p*-xylylene bromide with lead nitrate solution (Löw, Abstr., 1885, 1208, and others) than by the oxidation of *p*-xylene (Thiele and Winter, Abstr., 1900, i, 500) with chromic acid. The suggested oxidation of *p*-xylene by manganese dioxide and sulphuric acid (Lassar-Cohn, *Arbeitsmethoden*, 4th ed., 977) was found to yield *p*-toluic acid in place of the desired product.

When terepththalaldehyde is reduced by sodium amalgam in aqueous alcoholic solution, *p*-xylylene glycol is obtained, together with another *substance*, m. p. 220°.

Terephthalaldehydic acid is best obtained by oxidation of the dialdehyde with potassium dichromate and dilute sulphuric acid; its m. p. is 256° (compare Simonis, this vol., i, 565), but in an open tube appears to be higher on account of oxidation to terephthalic acid.

Nitration of terephthalaldehyde (compare Löw, *loc. cit.*) produces nitroterephthalaldehyde, m. p. 86° (*phenylhydrazone*, m. p. 213—216°; *tetracetate*, m. p. 147—149°), with two nitroterephthalaldehydic acids, m. p. 160° and 184° respectively, and a sparingly soluble *acid*, m. p. above 300°, as by-products.

The *methyl* ester of terephthalaldehydic acid, obtained by interaction of methyl iodide and the silver salt of the acid, crystallises in rods, m. p. 62—63°, and can be hydrolysed by alcoholic sodium hydroxide to the original acid; the ester gives a *phenylhydrazone*, yellow needles, m. p. 144—146° (in one experiment a substance, m. p. 116—117°, possibly a labile form, was obtained), a *diacetate*, rods, m. p. 66—68°, a *hydrobenzamide* compound, $N_2(CH{\cdot}C_6H_4{\cdot}CO_2Me)_3$, m. p. 140—142°, and is easily oxidised at 100° by air, giving methyl hydrogen terephthalate. When terephthalaldehydic acid is heated at 100° with methyl alcohol containing a little hydrogen chloride, the above methyl ester is produced, but at 140° a mixture of this ester with its *dimethylacetal* derivative, $CO_2Me{\cdot}C_6H_4{\cdot}CH(OMe)_2$, m. p. 29—30°, is obtained; in an impure condition the latter substance readily decomposes with formation of the methyl ester.

The ethyl ester of terephthalaldehydic acid, which has already been obtained by Löw (*loc. cit.*), is an oil which crystallises after long standing, possibly on account of oxidation.

Phosphorus pentachloride acts on terephthalaldehydic acid with the formation of *ω-dichloro*-p-*toluoyl chloride*, m. p. 50—52°. It was not found possible to convert the substance into the above acetal, but

by treatment with methyl alcohol containing suspended calcium carbonate, *methyl ω-dichloro-p-toluate*, m. p. 32—35°, was obtained. Attempts to prepare the free dichloro-acid were unsuccessful.

D. F. T.

Some New Derivatives of the Dihydroxybenzoic Acids. FRANZ VON HEMMELMAYR (*Monatsh.*, 1912, **33**, 971—998).—5-*Bromocatecholcarboxylic acid*, $C_7H_5O_4Br,H_2O$, is obtained when a solution of catecholcarboxylic (2 : 3-dihydroxybenzoic) acid in glacial acetic acid is treated with the requisite quantity of bromine at the ordinary temperature. It forms transparent, colourless, prismatic crystals, m. p. 185°. When the aqueous solution of these crystals is boiled for some time, it deposits, on cooling, white, silky, microscopic needles in addition to the prismatic crystals; these sinter at 211°, and have m. p. 215°. The *barium* salt, $(C_7H_4O_4Br)_2Ba,H_2O$, crystallises in clusters of flat needles.

4 : 5-Dibromocatecholcarboxylic acid (compare Praxmarer, Abstr., 1907, i, 216) is best obtained from the dihydroxybenzoic acid by bromination in glacial acetic acid solution. It forms long, colourless needles, m. p. 241° (decomp.). The *barium* salt, $(C_7H_3O_4Br_2)_2Ba,3H_2O$, forms spherular aggregates of slender needles. The *methyl* ester, $C_8H_6O_4Br_2$, crystallises in slender needles, m. p. 156—157°.

The two bromo-substitution products of β-resorcylic (2 : 4-dihydroxybenzoic) acid (compare Zehenter, Abstr., 1882, 193; 1887, 924) are best prepared, using glacial acetic acid as the solvent during bromination. Bromo-β-resorcylic acid has m. p. 212°; the dibromo-acid has m. p. 220°. *Dibromo-2 : 4-diacetoxybenzoic acid*, $C_{11}H_8O_6Br_2$, crystallises in slender prisms, m. p. 165°. Attempts to prepare the silver salt from the ammoniacal solution were unsuccessful, since the ammonia brings about partial fission of the acetyl group. The aqueous solution of the diacetyl acid is decomposed on boiling; to a slight extent the decomposition proceeds with evolution of carbon dioxide, but for the most part it takes place with fission of one acetyl group, giving *dibromoacetoxybenzoic acid*, $C_9H_6O_5Br_2$, which crystallises in bundle-shaped groups of needles, m. p. 195°.

By the action of nitric acid (D 1·4) on dibromo-β-resorcylic acid, 2-*bromo*-4 : 6-*dinitroresorcinol*, $C_6H_3O_6N_2Br$, is produced. It forms yellow, leaf-like crystals, and has m. p. 192·5°.

By the bromination of nitro-β-resorcylic acid in glacial acetic acid solution, even when sufficient bromine is used for the substitution of two hydrogen atoms, 3-*bromo*-5-*nitro*-β-*resorcylic acid*, $C_7H_4O_6NBr,2H_2O$, is obtained as yellow needles, m. p. 242° (decomp.). The basic *barium* salt ($6H_2O$) and *silver* salts are described. The *methyl* ester, $C_8H_6O_6NBr$, forms long, tabular crystals, m. p. 198—200°. It was not possible to bring about complete acetylation of the acid; treatment of the partly acetylated product with dilute ammonium hydroxide gave orange-red, microscopic prisms of the *diammonium* salt, $C_7H_{10}O_6N_3Br$.

4-*Bromo*-2 : 6-*dinitro*-α-*resorcylic acid*, $C_4H_3O_8N_2Br,1$ or $2H_2O$, is obtained from monobromo-α-resorcylic acid (Barth and Senhofer, Abstr., 1872, 1014) by the action of nitric acid (D 1·4), the temperature not being allowed to rise very much. It forms yellow, glistening leaflets,

m. p. 210° (decomp.). The basic *barium* salt ($2H_2O$) and two *silver* salts were prepared. When the acid is boiled with water, 2-bromo-4 : 6-dinitroresorcinol separates, owing to decomposition; when acetylated with acetic anhydride the carboxyl group is eliminated, and *bromodinitroresorcinol diacetate* $C_{10}H_7O_8N_2Br$, obtained as yellow needles, m. p. 113°.

2 : 4-*Dibromo-a-resorcylic acid*, $C_7H_4O_4Br_2,3H_2O$, is obtained by the bromination of α-resorcylic (3 : 5-dihydroxybenzoic) acid in glacial acetic acid solution. It crystallises in colourless, spherular aggregates of tabular crystals, m. p. 192°. The *barium* ($10H_2O$) and *silver* ($4H_2O$) salts are described. The *diacetyl* derivative, $C_{11}H_8O_6Br_2$, forms large, colourless crystals, m. p. 182—183°. Nitration of the acid with 1·4 nitric acid gives yellow needles of 2 : 4-*dibromo*-6-*nitro-a-resorcylic acid*, m. p. 208° (decomp.). The basic *barium* ($6H_2O$) and *silver* (H_2O) salts are described.

The aqueous solutions of the various acids mentioned above, together with those of 2 : 4-, 2 : 5-, 2 : 6- and 3 : 4-dihydroxybenzoic acids, nitro- and dinitro-2 : 4-dihydroxybenzoic acid, monobromo-2 : 5-, dibromo-2 : 6- and tribromo-3 : 4-dihydroxybenzoic acids were investigated with respect to the stability of the carboxyl group on boiling. With the exception of nitro-2 : 4-, monobromo-2 : 5-, monobromo-3 : 4-, 4 : 5-dibromo-2 : 3- and the 2 : 5- and 3 : 4-dihydroxybenzoic acids, more or less elimination of carbon dioxide takes place. T. S. P.

An α-Hydroxy-lactone from Phenylacetaldehyde. ERNST SPÄTH (*Monatsh.*, 1912, **33**, 1029—1054).—The author has found a second example of the characteristic condensation of an aldehyde with potassium cyanide previously observed with *iso*butaldehyde (Kohn, Abstr., 1899, i, 328).

An aqueous-alcoholic solution of a mixture of phenylacetaldehyde and potassium cyanide slowly deposits colourless needles of *β-hydroxy-αγ-diphenylbutaldehydecyanohydrin*,

$$CH_2Ph\cdot CH(OH)\cdot CHPh\cdot CH(OH)\cdot CN,$$

m. p. 146—148°; the mother liquor contains a brown, amorphous *substance*, $C_{32}H_{28}O(OH)_2$, the two hydroxyl groups being detected by Zerewitinoff's method (Abstr., 1907, ii, 509). The cyanohydrin is easily hydrolysed by dilute acids, preferably in alcoholic solution, the product being *α-hydroxy-β-phenyl-γ-benzylbutyrolactone*,

$$CO\!<\!\begin{matrix}O\text{———}CH\cdot CH_2H\\ CH(OH)\cdot CHPh\end{matrix},$$

needles, m. p. 114—115°, b. p. 264—265°/16 mm. (compare Erlenmeyer and Reis, Abstr., 1904, i, 1018); on warming with dilute potassium hydroxide solution the lactone is converted into sparingly soluble *potassium αγ-dihydroxy-βδ-diphenylvalerate*, m. p. 228° (decomp.), which at 250° in a vacuum decomposes with formation of αγ-diphenylpropylene (compare Dieckmann and Kämmerer, Abstr., 1906, i, 820). The lactone gives an oily *acetate* and a *benzoate*, m. p. 126—127°, which is also obtained by the action of benzoyl chloride and potassium hydroxide solution on the cyanohydrin.

The lactone shows the tendency to esterify to give esters of the corresponding hydroxy-acid, but by the action of methyl iodide on the

silver salt of the acid, *methyl αγ-dihydroxy-βδ-diphenylvalerate* was obtained in needles, m. p. 124—126° (decomp.); the *ethyl* ester, obtained in an analogous manner, forms needles, m. p. 122—123° (decomp.); both esters at 130° decompose quantitatively into the lactone and the corresponding alcohol.

On reduction of the lactone with hydriodic acid at 200°, a mixture of 2-phenylnaphthalene, leaflets, m. p. 101—102°, with an oil, b. p. 184—187°/14 mm., which is probably 2-*phenyltetrahydronaphthalene*, is obtained. With magnesium methyl iodide the lactone gives *αγ-diphenyl-ε-methylhexane-βδε-triol*, colourless crystals, m. p. 134—135°.

The lactone in warm alcoholic solution forms *additive* compounds with phenylhydrazine, hydrazine (applied as the hydrate), and methylamine, the products being of uncertain structure, and the m.p.'s 184° (decomp.), 184—185°, and 174—175° respectively. All three products are easily hydrolysed by dilute mineral acid into their constituents.

The cyanohydrin behaves similarly with the above three bases; phenylhydrazine produces colourless needles of *ε-imino-ε-phenylhydrazino-βδ-dihydroxy-αγ-diphenylpentane*,

$$CH_2Ph\cdot CH(OH)\cdot CHPh\cdot CH(OH)\cdot C(:NH)\cdot NH\cdot NHPh,$$

m. p. 142—147°, which when heated with aqueous alcohol loses the elements of water, giving a heterocyclic *substance*, $C_{23}H_{22}O_2N_2$, of uncertain structure, colourless needles, m. p. 184°; *hydrochloride*, sparingly soluble needles. Hydrazine and methylamine produce respectively *ε-imino-ε-hydrazino-βδ-dihydroxy-αγ-diphenylpentane*,

$$CH_2Ph\cdot CH(OH)\cdot CHPh\cdot CH(OH)\cdot C(:NH)\cdot NH\cdot NH_2,$$

m. p. 183—184°, and *ε-methylamino-ε-imino-βδ-dihydroxy-αγ-diphenylpentane*, a slowly solidifying syrup. The latter substance on cautious hydrolysis by keeping in cold aqueous alcoholic solution gives a product identical with the additive compound of the lactone and methylamine. These addition compounds of cyanohydrin with the above bases are all hydrolysable by mineral acids to the lactone and the corresponding base. D. F. T.

Preparation of 1-Aminoanthraquinone-2-carboxylic Acid and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 247411).—1-Aminoanthraquinone-2-carboxylic acid or its substituted derivatives are readily obtained by the action of ammonia or of primary or secondary amines on anthraquinone-2-carboxylic acids, which are negatively substituted in the α-position.

1-*Aminoanthraquinone-2-carboxylic acid*, yellow needles, m. p. 280°, is prepared by boiling 1-chloroanthraquinone-2-carboxylic acid (86 parts) and copper oxide (3 parts) with 300 parts of water and an equal quantity of 15% ammonium hydroxide solution during six hours under reflux; the *alkali* salts dissolve in water to form a red solution. *Methylaminoanthraquinone-2-carboxylic acid*, bluish-red needles, m. p. 240°, is obtained when the ammonium hydroxide in the foregoing example is replaced by methylamine; the *alkali* salts furnish bluish-coloured aqueous solutions.

1-*Anilinoanthraquinone-2-carboxylic acid*, glistening, brown leaflets, m. p. 297—298°, is prepared by boiling 1-nitroanthraquinone-2-carboxylic acid (86 parts) with aniline (860 parts).

1 : p'-*Chloroanilinoanthraquinone*-2-*carboxylic acid* is obtained as a red powder from *p*-chloroaniline and 1-chloroanthraquinone-2-carboxylic acid with copper oxide and sodium carbonate; the *sodium* salt separates in glistening, golden leaflets.

1-β-*Naphthylaminoanthraquinone*-2-*carboxylic acid* is a dark violet powder; its alkali salts are very sparingly soluble in water with a violet coloration; the *sodium* salt forms graphite-like crystals.

1-*Piperidylaminoanthraquinone*-2-*carboxylic acid* forms red flakes.

1-*Glycylanthraquinone*-2-*carboxylic acid*, red needles, is obtained by the action of sodium glycine on 1-chloroanthraquinone-2-carboxylic acid in the presence of copper powder in aqueous solution.

Nitro-1-β-*naphthylaminoanthraquinone*-2-*carboxylic acid*, a black powder, is prepared from 1-chloronitroanthraquinone-2-carboxylic acid and β-naphthylamine; the *sodium* salt separates as a dark violet powder, whilst the *compound* obtained by heating 1-chloroanthraquinone-2-carboxylic acid with 3-amino-*p*-toluoylbenzoic acid is a violet powder dissolving in alkali with a violet coloration.

The 1-*chloroanthaquinone*-2-*carboxylic acid* employed in these preparations was prepared by the oxidation of 1-chloro-β-anthraquinonealdehyde (Abstr., 1907, i, 224); it forms yellow needles and has m. p. 267°. F. M. G. M.

Preparation of Condensation Products Containing Sulphur in the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248996).—1-*Anilino*-4-p-*tolylthiolanthraquinone*-2-*carboxylic acid*, a bluish-violet powder, is prepared by condensing 4-chloro-1-anilinoanthraquinone-2-carboxylic acid with *p*-thiocresol; by further condensation it furnishes an *acridone*, which can also be obtained by the action of *p*-thiocresol on 4-chloroanthraquinone-2 : 1-acridone.

1-β-*Naphthylamino*-4-p-*tolylthiolanthraquinone*-2-*carboxylic acid*, a green powder, is obtained in a similar manner from 4-chloro-1-β-naphthylaminoanthraquinone-2-carboxylic acid, whilst 1 : 4-*di*-p-*tolylthiolanthraquinone*-2-*carboxylic acid*, a red powder, is prepared from 1 : 4-dichloroanthraquinone-2-carboxylic acid. These compounds are all readily converted into the corresponding *acridones*. F. M. G. M.

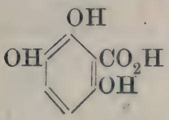
Action of Alkalis on Bisdiphenylacetylhydrazide Chloride. ROBERT STOLLÉ and F. SCHMIDT (*Ber.*, 1912, 45, 3113—3116).—On treatment with alcoholic sodium ethoxide at a low temperature, or when boiled with aqueous sodium hydroxide, bisdiphenylacetylhydrazide chloride, $CHPh_2{\cdot}CCl{:}N{\cdot}N{:}CCl{\cdot}CHPh_2$ (Abstr., 1911, i, 508), loses hydrogen chloride and is converted into tetraphenylsuccinonitrile. It is probable that the compound (I) $CPh_2{:}C{:}N{\cdot}N{:}C{:}CPh_2$ is intermediately formed in the reaction, but, owing to the instability of the group $C{:}C{:}N{\cdot}N{:}C{:}C$, at once undergoes rearrangement with the formation of the nitrile. That the rupture of the nitrogen-linking is not due to a special action of the alkali is shown by the behaviour of 3 : 6-bidiphenylmethylene-3 : 6-dihydro-1 : 2 : 4 : 5-tetrazine (see this vol., i, 1036). When heated alone or in solution, this loses nitrogen (1 mol.), yielding tetraphenylsuccinonitrile, the abovementioned compound (I) no doubt being formed as an intermediate

product. Insufficient cooling during the action of sodium ethoxide on the hydrazide chloride causes the formation of diphenylacetonitrile.

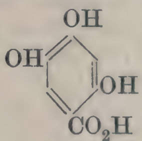
Tetrachlorotetraphenylsuccinonitrile, $C_{28}H_{16}N_2Cl_4$, prepared by chlorinating tetraphenylsuccinonitrile in the light of a mercury lamp, crystallises in stout prisms, m. p. 164°.

Phenyliminodiphenylacetyl chloride reacts with sodium methoxide, yielding *methyl phenyliminodiphenylacetate*, $C_{21}H_{19}ON$, crystallising in colourless needles, m. p. 150°. The *ethyl* ester, prepared in a similar manner, forms prisms, m. p. 131°. F. B.

Some Derivatives of Hydroxyquinol. VIII. GUIDO BARGELLINI and ERMANNO MARTEGIANI (*Gazzetta*, 1912, **42**, ii, 351—356. Compare this vol., i, 292).—The hydroxyquinolcarboxylic acid of Thiele and Jäger has been stated by von Hemmelmayr (Abstr., 1911, i, 983) to have the constitution (I), but the authors now advance evidence in favour of formula (II). When the acid is treated with methyl sulphate, asaronic acid is formed (compare Fabinyi and Széki, Abstr., 1907, i, 45), and the position of the methoxyl groups in this compound is established by the fact that it can be obtained by oxidation of 2 : 4 : 5-trimethoxyacetophenone. The esterification of the hydroxyquinolcarboxylic acid with methyl sulphate does not proceed quantitatively, for hydroxyquinol trimethyl ether and hexamethoxydiphenyl are also formed.

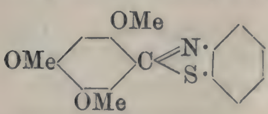


(I.)

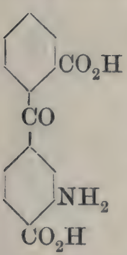


(II.)

Asaronanilide, $C_{16}H_{17}O_4N$ (prepared with phenylcarbimide), forms dirty white scales, m. p. 144—146°. *Asaronthioanilide*, $C_{16}H_{17}O_3NS$, is a yellow crystalline substance, m. p. 159—160°. When it is treated in alkaline solution with potassium ferricyanide, an oxidation product, $C_{16}H_{15}O_3NS$, is obtained. It is a yellow substance, m. p. 193—195°, and to it is assigned the constitution of 2 : 4 : 5-*trimethoxyphenylbenzthiazole* (annexed formula). R. V. S.



Preparation of *o*-Aminoanthraquinonecarboxylic Acid. ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 248838).—When o-*aminocarboxybenzoyl*-o-*benzoic acid* (annexed formula) is heated with sulphuric acid or other condensing reagents it usually yields about 70% of 3-aminoanthraquinone-2-carboxylic acid with 30% of 1-*aminoanthraquinone-2-carboxylic acid*, red crystals, m. p. 280° (about); the separation of these products is effected by means of the relative insolubility of sodium 3-aminoanthraquinone-2-carboxylate in excess of alkali.



Nitroterephthaloyl-o-*benzoic acid* and o-*aminoterephthaloyl*-o-*benzoic acid*, yellow leaflets, m. p. 265°, were also obtained during the preparation of the foregoing *o*-aminocarboxybenzoyl-*o*-benzoic acid from *p*-toluoyl-*o*-benzoic acid (Abstr., 1898, i, 322). F. M. G. M.

Constitution of Orsellinic Acid. ALFRED THIEL (*Annalen*, 1912, **394**, 108—110).—A proof that one hydroxyl group in orsellinic acid is in the para-position to the carboxyl group (Fischer and Hoesch, this vol., i, 859) has already been given by Thiel, Schumacher, and Roemer (Abstr., 1906, i, 22). C. S.

Preparation of Halogen Derivatives of Benzaldehyde. JAN J. BLANKSMA (*Chem. Weekblad*, 1912, **9**, 862—870. Compare Abstr., 1909, i, 936).—A number of halogen derivatives of benzaldehyde have been prepared from ring-substituted *p*-aminobenzaldehydes. Aniline converts 3 : 5-dibromo-4-aminobenzaldehyde into 3 : 5- *dibromo*-4-*aminobenzylideneaniline*, $C_6H_5 \cdot N:CH \cdot C_6H_2Br_2 \cdot NH_2$, pale yellow crystals, m. p. 99°. Diazotisation of 3 : 5-dibromo-4-aminobenzaldehyde in hydrobromic acid and treatment with cuprous bromide in the same solvent yields 3 : 4 : 5-*tribromobenzaldehyde* in colourless crystals, m. p. 108°, readily sublimed and volatile in steam. Boiling with aqueous potassium permanganate converts it into 3 : 4 : 5-tribromobenzoic acid, m. p. 235° (compare Sudborough, Abstr., 1894, i, 244); acetic anhydride and concentrated sulphuric acid give a *diacetyl* derivative, $C_6H_2Br_3 \cdot CH(OAc)_2$, colourless crystals, m. p. 100°; aniline produces 3 : 4 : 5-*tribromobenzylideneaniline*, colourless crystals, m. p. 99°; *p*-toluidine forms 3 : 4 : 5-*tribromobenzylidene*-p-*toluidine*, m. p. 98°.

Bromine water converts 2-bromo-4-aminobenzaldehyde into 2 : 3 : 5-*tribromo*-4-*aminobenzaldehyde*, m. p. 182°, which is converted by diazotisation in sulphuric acid into 2 : 3 : 5-*tribromobenzaldehyde*, colourless crystals, m. p. 114°, volatile with steam, and by aqueous potassium permanganate into 2 : 3 : 5-tribromobenzoic acid, m. p. 187° (compare Rosanoff and Prager, Abstr., 1909, ii, 32; Ullmann and Kopetschni, Abstr., 1911, i, 292).

m-Aminobenzaldehyde is transformed by bromine water into 2 : 4 : 6-tribromo-*m*-aminobenzaldehyde, m. p. 139° (compare Anilinfarben- & Extrakt-Fabriken, vormals J. R. Geigy, Abstr., 1910, i, 175), from which diazotisation yields 2 : 4 : 6-*tribromobenzaldehyde*, colourless crystals, m. p. 99°, volatile with steam; it is converted by potassium permanganate into 2 : 4 : 6-tribromobenzoic acid, m. p. 186°; and by aniline into 2 : 4 : 6-*tribromobenzylideneaniline*, pale yellow needles, m. p. 90°.

Diazotisation and treatment with cuprous bromide in hydrobromic acid convert 2 : 4 : 6-tribromo-4-aminobenzaldehyde into 2 : 3 : 4 : 6-*tetrabromobenzaldehyde*, a colourless substance volatile with steam, m. p. 116°, which is transformed by warming with aniline into 2 : 3 : 4 : 6-benzylideneaniline, m. p. 108°.

On nitration, *p*-acetylaminobenzaldehyde yields 3-nitro-*p*-acetylaminobenzaldehyde, m. p. 155°, which is saponified to 3-nitro-4-aminobenzaldehyde, m. p. 190° (compare Cohn and Springer, Abstr., 1903, i, 492), a substance converted by bromine water into 3-*bromo*-5-*nitro*-4-*aminobenzaldehyde*, pale yellow crystals, m. p. 168°, or by excess of bromine water into 2 : 4-dibromo-6-nitroaniline, m. p. 127°. On diazotisation, 3-bromo-5-nitro-4-aminobenzaldehyde is converted into 3-*bromo*-5-*nitrobenzaldehyde*, pale yellow needles volatile with steam,

m. p. 100°, which is oxidised by potassium permanganate to 3-bromo-5-nitrobenzoic acid, colourless crystals, m. p. 162°.

With bromine water, 3-bromo-5-aminobenzaldehyde yields 2 : 4 : 5 : 6-*tetrabromo-3-aminobenzaldehyde*, pale yellow needles, m. p. not below 270°, which is converted by Sandmeyer's method into *pentabromobenzaldehyde*, colourless crystals, m. p. not below 270°. This substance is oxidised by potassium permanganate to pentabromobenzoic acid colourless crystals, m. p. 252° (not 235° as given by Reinecke, *Zeitsch. Chem.*, 1869, 110).

3-Nitro-4-aminobenzaldehyde is converted by Sandmeyer's reaction into 4-chloro-3-nitrobenzaldehyde, colourless crystals, m. p. 65°, oxidised by potassium permanganate to 4-chloro-3-nitrobenzoic acid, m. p. 178°. The corresponding bromo-derivative is prepared similarly, has m. p. 106°, and is oxidised by potassium permanganate to 4-bromo-3-nitrobenzoic acid, m. p. 199°.

3-Bromo-5-nitro-4-aminobenzaldehyde yields by Sandmeyer's method 3 : 4-*dibromo-5-nitrobenzaldehyde*, colourless crystals, m. p. 99°, oxidised by potassium permanganate to 3 : 4-dibromo-5-nitrobenzoic acid, colourless crystals, m. p. 183°.

Bromine water reacts with 2-chloro-4-aminobenzaldehyde, forming 2-*chloro*-3 : 6-*dibromo*-4-*aminobenzaldehyde*, pale yellow needles, m. p. 174°, which by Sandmeyer's method yields 2-*chloro*-3 : 4 : 5-*tribromobenzaldehyde*, colourless crystals, m. p. 121°.

2-Chloro-4-acetylaminobenzaldehyde is converted by nitric acid into 2-*chloro*-5-*nitro*-4-*acetylaminobenzaldehyde*, pale yellow crystals, m. p. 98°. Elimination of the acetyl group by concentrated hydrochloric acid produces 2-*chloro*-5-*nitro*-4-*aminobenzaldehyde*, yellow crystals, m. p. 194°, which is converted by Sandmeyer's method into 2 : 4-dichloro-5-nitrobenzaldehyde, m. p. 74° (compare Anilinfarben- & Extrakt Fabriken vormals J. R. Geigy, D.R.-P. No. 198809).

A. J. W.

Asymmetric Synthesis Produced by the Action of Catalysts. Georg Bredig and P. S. Fiske (*Biochem. Zeitsch.*, 1912, **46**, 7—23).—Under the influence of optically active alkaloids as catalysts, benzaldehyde cyanohydrin can be produced by the interaction of benzaldehyde and hydrocyanic acid, the alkaloid acting in a similar way to emulsin in this respect. When quinine is employed, the product of the asymmetric synthesis is dextrorotatory, and yields a lævorotatory mandelic acid, whereas under the influence of quinidine the products of reaction show the rotations in the reverse directions. As the molar amounts of alkaloids necessary to produce the reactions are less than those of the products produced, the action must be of catalytic character. The alkaloids appear to enter into combination with the cyanohydrins, as they cannot be removed from solutions in organic solvents containing both alkaloid and cyanohydrin by simply washing with strong aqueous hydrochloric acid; indeed, such solutions in inorganic solvents can remove the alkaloid from a solution of its hydrochloride in water.

S. B. S.

Synthesis of Aromatic Aldehydes. III. LUDWIG GATTERMANN (*Annalen*, 1912, 393, 215—233. Compare Abstr., 1906, i, 589; 1908, i, 28).—Many aromatic aldehydes which cannot be prepared by either of the author's earlier methods have been obtained by the interaction of magnesium aryl haloids with ethyl formate or ethoxymethyleneaniline in ether, preferably at $-50°$. The yields are in many cases less than 10%, but at times, especially at low temperatures, exceed 60% of the theoretical.

The two processes are as follows: The cold ethereal solution of the magnesium aryl haloid is slowly added to a cold ethereal solution of ethyl formate. After the reaction, the mixture is acidified with cold hydrochloric acid, the ether and the excess of ethyl formate are removed on the water-bath, and the aldehyde is then distilled with steam and purified through the sodium hydrogen sulphite compound. The method with ethoxymethyleneaniline is performed thus: the ethereal solution of the magnesium aryl haloid is heated just to boiling, and is slowly treated with an ethereal solution of ethoxymethyleneaniline (prepared from the dry silver salt of formanilide and ethyl iodide), the mixture is cooled after the reaction, acidified with dilute hydrochloric acid, and is then treated as above for the isolation and purification of the aldehyde.

o-Tolualdehyde is obtained from *o*-bromotoluene in 50% and 55% yield respectively by the ethyl formate and ethoxymethyleneaniline methods. 2:5-*Dimethylbenzaldehyde*, $C_6H_3Me_2 \cdot CHO$, b. p. 219—220°/738 mm., colourless, pleasantly odorous liquid, obtained in 45% yield from bromo-*p*-xylene by the ester method at $-60°$, yields 2:5-*dimethylcinnamic acid*, m. p. 128·5°, by Claisen's method, and reacts with acetone to form 2:5-*dimethylstyryl methyl ketone*, $C_{12}H_{14}O$, b. p. 154—156°/15 mm. (*azine*, $C_{24}H_{28}N_2$, m. p. 163°, yellow needles; *semicarbazone*, $C_{13}H_{17}ON_3$, m. p. 204°, colourless needles; *dibromo*-additive compound, $C_{12}H_{14}OBr_2$, m. p. 128°, colourless leaflets). It is extremely remarkable that the nitration of 2:5-dimethylbenzaldehyde by potassium nitrate and concentrated sulphuric acid at about $-15°$ yields 6-*nitro*-2:5-*dimethylbenzaldehyde*, m. p. 120°, yellow needles or leaflets. The nitrated aldehyde forms an *azine*, $C_{18}H_{18}O_4N_4$, m. p. 162°, yellow needles; *semicarbazone*, m. p. 183°, colourless needles, yields *tetramethylindigotin*, blue needles, by treating its alcoholic solution with acetone and aqueous sodium hydroxide, and forms 6-*amino*-2:5-*dimethylbenzaldehyde*, m. p. 52°, amber crystals, by reduction with ferrous sulphate and aqueous ammonia.

p-Bromobenzaldehyde, obtained from *p*-dibromobenzene in 40% yield by the ester method at $-50°$, forms a *phenylhydrazone*, m. p. 112—113°, brownish-yellow needles; *azine*, m. p. 221°, long, yellowish-green leaflets, and *acetal*, m. p. 89—90°, yellow crystals.

4-*Bromo*-2:5-*dimethylbenzaldehyde*, m. p. 63·5°, needles or leaflets, obtained in 10% yield from 2:5-dibromo-*p*-xylene at $-50°$ by the ester method, forms an *azine*, m. p. 219°, green needles, and *oxime*, m. p. 113°, colourless needles.

o-*Ethoxybenzaldehyde*, obtained in 30% yield from *o*-bromophenetole by the ester method at $-60°$, forms an *azine*, m. p. 136°, yellow crystals, and *semicarbazone*, m. p. 219°, long, colourless needles

condenses with benzidine to form *di*-o-*ethoxybenzylidenebenzidine*, m. p. 137—138°, large leaflets, reacts with magnesium phenyl bromide to form ultimately o-*ethoxybenzhydrol*, m. p. 75°, stout, colourless crystals, and yields by nitration with potassium nitrate and concentrated sulphuric acid at 0° *nitro*-o-*ethoxybenzaldehyde*, m. p. 69° (*azine*, m. p. 284—285°, yellow leaflets; *semicarbazone*, m. p. 223°, pale yellow prisms; *phenylhydrazone*, m. p. 203—204°, red needles).

p-*Methylthiolbenzaldehyde*, C_8H_8OS, m. p. 78°, yellow leaflets, obtained only by the ethoxymethyleneaniline method from *p*-iodophenyl methyl sulphide in about 60% yield, forms an *azine*, m. p. 193°, yellow leaflets; *semicarbazone*, m. p. 213°, colourless needles; *phenyl hydrazone*, m. p. 136°, yellow leaflets, and condensation *product*, $C_{15}H_{15}NS_2$, m. p. 145°, with *p*-thioanisidine, and yields p-*methylthiolbenzoic acid*, m. p. 190°, by oxidation with potassium permanganate.

p-*Ethylthiolbenzaldehyde*, b. p. 244—245°, yellow oil, obtained in a similar manner from *p*-iodophenyl ethyl sulphide in 32% yield, forms an *azine*, m. p. 151—152°, yellow leaflets; *phenylhydrazone*, m. p. 115°, colourless leaflets; *semicarbazone*, m. p. 193°, colourless needles, and condensation *product*, $C_{17}H_{19}NS_2$, m. p. 114—115°, yellow leaflets, with *p*-thiophenetidine.

α-Naphthaldehyde is obtained from α-bromonaphthalene in 45—50% yield by the ethoxymethyleneaniline method; it forms a *semicarbazone*, m. p. 221°, colourless needles, and condensation *product* with benzidine, $C_{34}H_{24}N_2$, m. p. 199°, yellow leaflets. β-Naphthaldehyde, obtained in 40% yield in a similar manner, forms an *azine*, m. p. 232°, yellow needles, *phenylhydrazone*, m. p. 205—206° (decomp.), colourless leaflets, *semicarbazone*, m. p. 245°, colourless needles, and *β-naphthylideneaniline*, m. p. 113°; with malonic acid and alcoholic ammonia it forms *β-naphthylacrylic acid*, $C_{10}H_7\cdot CH\colon CH\cdot CO_2H$, m. p. 203°, colourless needles, from which *β-naphthylpropionic acid*, m. p. 129—130°, colourless leaflets, is obtained by reduction with sodium amalgam.

Bromothiophenaldehyde, a yellow oil with the odour of bitter almonds, is obtained in about 10% yield from dibromothiophen by the ester method; it forms an *azine*, m. p. 157—158°, yellow needles, *semicarbazone*, m. p. 200—201°, colourless leaflets, and *phenylhydrazone*, m. p. 105°, colourless leaflets, and yields the acid, m. p. 139·5°, by oxidation.

Bromothiophen is obtained in 70% yield by converting dibromothiophen into magnesium bromothiophen bromide, and treating this with hydrochloric acid in the cold. Thiophenaldehyde, obtained from it in 15% yield by the ester method at −20°, forms an *azine*, $C_{10}H_8N_2S_2$, m. p. 154°, long, yellow needles.

p-Nitrophenyl mercaptan, obtained from *p*-chloronitrobenzene and potassium hydrosulphide in boiling alcohol, is converted by alcoholic sodium methoxide and methyl iodide on the water-bath into p-*nitrophenyl methyl sulphide*, $NO_2\cdot C_6H_4\cdot SMe$, m. p. 72°, long, yellow plates. By reduction with tin and hydrochloric acid it yields p-*aminophenyl methyl sulphide*, b. p. 272—273°, which forms an *acetyl* derivative, m. p. 130·5°, colourless needles, and *benzoyl* derivative, m. p. 177—178°, leaflets, and is converted into p-*bromophenyl methyl sulphide*, m. p. 38°,

and p-*iodophenyl methyl sulphide*, m. p. 45°, by diazotisation and the usual subsequent treatment.

p-*Aminophenyl ethyl sulphide*, b. p. 280—281°, yellow oil, obtained from p-*nitrophenyl ethyl sulphide*, m. p. 44°, long, yellow needles, forms an *acetyl* derivative (*thiophenacetin*), m. p. 116—117°, colourless needles, and is converted into p-*iodophenyl ethyl sulphide*, b. p. 146—147°/11 mm., by the usual process. C. S.

A Colour Reaction of Unsaturated Ketones. GUSTAVE REDDELIEN (*Ber.*, 1912, **45**, 2904—2908).—$\alpha\beta$-Unsaturated ketones dissolve in concentrated sulphuric acid with the formation of intensely-coloured solutions, which when sufficiently dilute show a characteristic colour change on the addition of a small quantity of nitric acid. Other substances, such as water, hydrochloric acid, hydrobromic acid, bromine water, hydrogen peroxide, or phosphoric acid, do not cause an analogous change. The behaviour of nitric acid appears to be independent of the concentration (from D 1·5 to 1/10-*N*), and the colour change once effected is not altered by further gradual addition of nitric acid provided a rise of temperature is avoided. The phenomenon seems to depend on the instantaneous nitration of the unsaturated ketone and the feebler halochromy (compare Pfeiffer, Abstr., 1910, i, 852; *ibid.*, 1911, i, 788) of the nitro-ketones compared with the ketones themselves. The ready nitration of unsaturated ketones is doubtless connected with the ready addition of nitric acid to form nitrates, and the quantitative transformation of the latter into the corresponding nitro-compounds on solution in concentrated sulphuric acid.

To some extent this reaction is also shown by saturated ketones, such as acetophenone and benzophenone. In these cases, however, the substances are dissolved by concentrated sulphuric acid with the production of solutions so feebly coloured that a colour change can scarcely be detected. Readily oxidisable substances also show the reaction, but the colour change is then dependent on the quantity of nitric acid added. Certain readily oxidisable unsaturated ketones (for example, pulegone, carvenone, carvone) also show this reaction.

In practice, a trace of the ketone is dissolved in concentrated sulphuric acid (10 c.c.) and the solution divided into two parts. To one of these, a drop of nitric acid (D 1·4) is added. To the other, a drop of nitric acid (10%). The colorations produced must be similar. A considerable number of examples are cited.

Distyryl ketone nitrate, $C_{17}H_{14}O, HNO_3$, was obtained in orange-coloured crystals, m. p. 48—49°, by the addition of finely powdered distyryl ketone to nitric acid (D 1·4) at 50—55°. When preserved, it gradually lost nitric acid.

Phenyl styryl ketone nitrate, $C_{15}H_{12}O \cdot HNO_3$, was formed as a reddish-yellow oil by addition of the ketone to nitric acid (D 1·4) at the ordinary temperature.

Styryl methyl ketone nitrate was a pale yellow oil, which, when placed over nitric acid, absorbed nearly an additional molecule of the latter.

Cinnamylideneacetophenone nitrate, $C_{17}H_{14}O, HNO_3$, was obtained as a dark red, viscous, difficulty decomposed oil. H. W.

Supposed Isomerism in the Case of Methyl-Δ^1-*cyclo*hexene-3-one. PAUL RABE and ERNEST POLLOCK (*Ber.*, 1912, **45**, 2924—2927).—Knoevenagel (Abstr., 1897, i, 606) and Rabe and Ehrenstein (Abstr., 1907, i, 626) have stated that methyl-Δ^1-*cyclo*hexene-3-one exists in two isomeric forms, one of which is readily, the other sparingly, soluble in water. Further investigation has shown that this is not the case. Methyl-Δ^1-*cyclo*hexene-3-one is miscible with water at the ordinary temperature, whilst the sparingly soluble isomeride consists of different substances, which have not yet been fully investigated.

Specimens which are not completely soluble in water (previously termed β-methyl*cyclo*hexenone) can only be obtained by treatment of the oily ethyl methylenebisacetoacetate with 10% sulphuric acid. By systematic fractional solution of the sparingly soluble portion in water, a small quantity of an oil, b. p. 198—210°/750 mm., was obtained, analysis of which showed it to contain an excess of 6% of carbon and 1% of hydrogen above that required for methyl-Δ^1-*cyclo*hexene-3-one.

For the preparation of the latter substance in a pure state, the authors now recommend the decomposition of methyl*cyclo*hexanolone-dicarboxylic esters by potassium hydroxide instead of by sulphuric acid (*loc. cit.*). The following physical constants are given for the ketone (Roy, *Diss.*, Jena, 1910): m. p. ca $-21°$, n_D^{20} 1·49475, $n_{H_\alpha}^{20}$ 1·49005, $n_{H_\beta}^{0}$ 1·50522, $n_{H_\gamma}^{20}$ 1·51465; η^{20} 0·01763; dielectric constant, K 24·32; electrical conductivity of the pure substance, x_{20} $2·321 \times 10^{-7}$; mol. heat of combustion, 942·8 Cal. at constant volume, 944·0 Cal. at constant pressure.

Aqueous ferric chloride solution oxidises the ketone to *m*-cresol, whilst reduction by hydrogen in the presence of palladium yields methyl*cyclo*hexanone. The previous observations (*loc. cit.*) concerning the sodium salt of the ketone are withdrawn. H. W.

Some Derivatives of 3 : 4-Dimethoxypropiophenone. ERMANNO MARTEGIANI (*Gazzetta*, 1912, **42**, ii, 346—350. Compare Bargellini and Martegiani, Abstr., 1911, i, 854).—3 : 4-Dimethoxypropiophenone (identical with that of Hell and Portmann, Abstr., 1895, i, 657) is obtained from propionyl chloride and veratrole in the presence of aluminium chloride. Another substance, probably propionylguaiacol, may be formed also. The *oxime*, $C_{11}H_{15}O_3N$, crystallises in small, colourless, prismatic needles, m. p. 63—65°. The *semicarbazone*, $C_{12}H_{17}O_3N_3$, forms colourless needles, m. p. 190—192°. The *phenylhydrazone*, m. p. 108—110°, is a yellow, crystalline powder, which rapidly alters even in dry air.

The *monoxime*, $C_6H_3(OMe)_2 \cdot CO \cdot CMe \vdots NOH$ (prepared with amyl nitrite), forms colourless needles, m. p. 161—162°. From it the diketone could not be obtained. The substance yields veratric acid when boiled with an excess of amyl nitrite. The dioxime is identical with the β-dioxime which Malagnini obtained from di*iso*nitrosomethyl-*iso*eugenol peroxide (Abstr., 1895, i, 35). The *oximephenylhydrazone*, $C_{17}H_{19}O_3N_3$, crystallises in woolly needles, and has m. p. 209°. It dissolves in sulphuric acid, giving a yellowish-green coloration.

R. V. S.

Replacement of Oxygen in Ketones and Aldehydes by Hydrogen. LUDWIG WOLFF (*Annalen*, 1912, **394**, 86—108).—The semicarbazones of certain ketones are converted by aqueous sodium hydroxide at 150° into the hydrocarbons corresponding with the ketones, hydrazones being formed as intermediate products. Some hydrazones, therefore, are converted into hydrocarbons in a similar manner; others yield azines. When heated with an absolute alcoholic solution of sodium ethoxide, the hydrazones and semicarbazones of all aliphatic, aromatic, and cyclic ketones and aldehydes, and of ketonic acids are converted into hydrocarbons corresponding with the parent carbonyl compound, in 75—90% yield. The course of the reaction is represented by the scheme:

$$>C\colon N\cdot NH\cdot CO\cdot NH_2 \longrightarrow >C\colon N\cdot NH_2 \longrightarrow >CH_2 + N_2.$$

The amount of sodium ethoxide which apparently acts catalytically is of little importance. For the decomposition of semicarbazones, 96—98% alcohol can be employed. The temperature at which the decomposition is effected varies within wide limits. Generally, heating at 160° for six to eight hours is sufficient; the hydrazones of cyclic ketones require a higher temperature (up to 200°) or more prolonged heating. Similar decompositions have not been observed with phenylhydrazones.

[With GERHARD WEILAND.]—Benzophenonesemicarbazone or hydrazone and 7% aqueous alcoholic sodium hydroxide yield diphenylmethane at 150—160°. Acetophenonehydrazone or semicarbazone and alcoholic sodium ethoxide at 180° yield ethylbenzene. By similar means *p*-aminoacetophenonehydrazone yields *p*-aminoethylbenzene, dibenzyl ketone hydrazone yields dibenzylmethane, and the hydrazone of Michler's ketone yields *p*-dimethylaminodiphenylmethane.

[With E. THIELEPAPE.]—Hexane is obtained from the hydrazone or semicarbazone of methyl butyl ketone, menthane from menthonehydrazone, and camphane from camphorhydrazone.

[With E. NOLTE.]—Fenchone and hydrazine hydrate at 210° yield *fenchonazine*, $C_{20}H_{32}N_2$, m. p. 106—107°, and *fenchonehydrazone*, $C_{10}H_{18}N_2$, m. p. 56—57°, b. p. 230—231° (decomp.), $[\alpha]_D$ 46·4°, in 11% alcoholic solution; the latter is converted quantitatively by alcoholic sodium ethoxide at 180° in twenty hours into *fenchane*, $C_{10}H_{18}$, b. p. 149°, D_4^{20} 0·8316, n_D^{20} 1·4462, $[\alpha]_D$ −18·11° in alcohol.

[With HANS MAYEN.]—Ethyl lævulate and hydrazine hydrate yield hydrated 3-methyl-6-pyridazinone (Curtius's lævulic acid hydrazide), $C_5H_8ON_2,H_2O$, m. p. 82—83°. The anhydrous substance has m. p. 104—105° (not 94° as given by Curtius), b. p. 267°. The hydrated compound and alcoholic sodium ethoxide at 170—180° yield valeric acid.

Anisaldehydesemicarbazone yields anisazine and a little *p*-tolyl methyl ether by heating with alcoholic sodium hydroxide at 160°; the latter is obtained in larger yield by using alcoholic sodium ethoxide at 170°. By similar methods vanillinsemicarbazone yields the azine and 3-methoxy-*p*-cresol. *Furfuralhydrazone*, b. p. 105—110°/12 mm., and hot alcoholic sodium ethoxide yield 2-methylfuran, b. p. 62·5—63°/746 mm., D^{21} 0·912.

[With E. THIELEPAPE.]—By heating with hydrazine hydrate,

citronellal yields *citronellalazine*, b. p. 209—213°/15 mm,, and *citronellalhydrazone*, $C_{20}H_{36}N_2$, b. p. 125—140°/15 mm. The latter, which is better obtained from hydrazine hydrate at 160°, reacts with alcoholic sodium ethoxide at 170° to form citronellol and *βζ-dimethyl-Δ^a-octene*, CH_2:CMe·$[CH_2]_3$·CHMeEt (assuming that a shifting of the double linking does not occur), b. p. 162°, D_4^{20} 0·7558, n_D^{20} 1·4303, $[\alpha]_D^{20}$ 9·27° in alcoholic solution.

[With H. MAYEN.]—By heating with alcoholic sodium ethoxide at 165° for twenty hours, benzaldehydephenylhydrazone yields ammonia, aniline, benzoic acid, and a little acetic acid. At 210°, ethylaniline is also formed. When the phenylhydrazone is gently boiled for half an hour, it decomposes into ammonia, stilbene, aniline, benzaldehyde, and benzonitrile. In a similar manner, furfuralphenylhydrazone and alcoholic sodium ethoxide yield ammonia, aniline, and pyromucic acid; benzophenonephenylhydrazone yields ammonia, aniline, ethylaniline, diphenylcarbinol, acetic acid, and tetraphenylethane, and acetophenonephenylhydrazone yields ammonia, aniline, phenylmethylcarbinol, acetic acid, and 2-phenylindole, the last in 40% yield. C. S.

Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. VIII. So-called Keto-haloids of Unsaturated Ketones and their Transformation Products. FRITZ STRAUS (*Annalen*, 1912, **393**, 235—337. Compare Abstr., 1910, i, 563, 565).—The author has found that the keto-chlorides of unsaturated ketones undergo an apparently simple and smooth substitutive change, namely the replacement of the halogen by a methoxy-group, yielding products which can have been formed only by a complicated re-distribution of the double linkings. All previous conclusions based on processes of substitution therefore become uncertain. The mutual relations between keto-chlorides and their transformation products must be tested by reactions in which it is certain that the first step is addition at a double linking.

Dichlorodistyrylmethane, obtained by the action of phosphorus pentachloride (Abstr., 1906, i, 859) or of oxalyl chloride (Staudinger, Abstr., 1909, i, 905) on distyryl ketone, is reconverted into the ketone by hydrolysis. Both reactions are processes of substitution in an unsaturated ketone; therefore, the constitution of the keto-chloride is not safely established by them. By treating the keto-chloride in carbon tetrachloride at −15° to −10° with 9—10% ozone and decomposing the resulting ozonide with water, the author has obtained benzaldehyde, benzoic acid, α-chlorophenylacetaldehyde (isolated as its hydrolysed derivative, benzoylcarbinol), and α-chlorophenylacetic acid (isolated as α-methoxyphenylacetic acid). Consequently the keto-chloride of distyryl ketone is not dichlorodistyrylmethane as hitherto supposed, but *γε-dichloro-αε-diphenyl-Δ^{αγ}-pentadiene*,

CHPh:CH·CCl:CH·CHPhCl.

By similar fissive decomposition, the ozonide of the keto-chloride of phenylstyryl ketone yields benzoic acid, α-chlorophenylacetic acid, benzaldehyde, mandelic acid, benzoylcarbinol, and benzoyl chloride; the ozonide of the keto-chloride of cinnamylideneacetophenone yields the same products. The keto-chlorides of phenyl styryl ketone and

cinnamylideneacetophenone therefore have the constitutions

CHPhCl·CH:CPhCl

and CHPhCl·CH:CH·CH:CPhCl respectively. Also the keto-chloride of dicinnamylideneacetone has the constitution,

CHPhCl·CH:CH·CH:CCl·CH:CH·CH:CHPh,

containing a system of four conjugated double linkings. (In the fissive decomposition of the preceding ozonides, glyoxal [isolated as the *p*-nitrophenylosazone] is always obtained, being formed probably by the rupture of a benzene nucleus, and oxalic acid is produced when the keto-chloride contains a system of conjugated ethylenic linkings.) Cinnamylidene dichloride has the customary constitution

$CHPh:CH·CHCl_2$

because the decomposition of its ozonide by water results in the formation of benzoic acid and benzaldehyde, dichloroacetic acid and dichloroacetaldehyde, and glyoxal.

In view of the large number of additive compounds of metallic chlorides and carbonyl compounds now known, the author is of opinion that the initial reaction between an aldehyde or ketone and phosphorus pentachloride is the formation of a complex,

$RR^1C:O \ldots PCl_5$,

which subsequently changes to $RR^1CCl·OPCl_4$, and finally to

$RR^1CCl_2 + POCl_3$.

Similar schemes are advanced to explain the conversion of acids and their esters or their amides into acid chlorides or iminochlorides respectively by phosphorus pentachloride. In the cases of the preceding unsaturated ketones containing conjugated double linkings, the primary additive compound containing the group

$·CH:CH·\dot{C}:O \ldots PCl_5$

or $·CH:CH·CH:CH·\dot{C}:O \ldots PCl_5$ changes, by a transference of chlorine to the other extremity of the conjugated system, to a substance containing $·CHCl·CH:\dot{C}·OPCl_4$ or

$·CHCl·CH:CH·CH:\dot{C}·OPCl_4$,

from which the final product is obtained by the elimination of phosphoryl chloride. The formation of the same (so-called) keto-chlorides from the preceding unsaturated ketones and oxalyl chloride can be explained in a similar manner by assuming that the acid chloride is first attached to the carbonyl oxygen atom of the ketone by means of its residual affinity, the resulting additive compound then undergoing changes analogous to those given above. With the former view of the constitution of keto-chlorides, one difficulty in explaining the replacement of the halogen lies in the fact that, although both chlorine atoms are similarly bound, only one enters into substitutive reactions. Another difficulty arises in connexion with the varying additive activity of the ethylenic linkings; the keto-chloride of distyryl ketone contains, according to the old formulation, two exactly similar double linkings, yet the substance reacts additively only with one molecule of bromine. These difficulties disappear with the acceptance of the constitution of keto-chlorides now advanced. (The name keto-chloride is retained for brevity.)

Keto-chlorides react rapidly with water or methyl alcohol, one chlorine atom being replaced by the hydroxyl or methoxy-group with the formation of the (so-called) chlorocarbinols or their methyl ethers; from these the keto-chlorides are regenerated by hydrochloric acid. Hitherto these reactions have been regarded as a simple direct replacement of chlorine by hydroxyl or methoxyl, and vice versâ,

$$CCl_2(CH:CHPh)_2 \underset{HCl}{\overset{H_2O}{\rightleftarrows}} OH\cdot CCl(CH:CHPh)_2.$$

However, by oxidising the methyl ethers of the preceding keto-chlorides (of distyryl ketone, cinnamylideneacetophenone, dicinnamylideneacetone) in acetone by potassium permanganate at 15—20° a constant product of the oxidation is α-methoxyphenylacetic acid. Consequently they all contain the group OMe·CHPh·CH:C, and the keto-chlorides themselves, therefore, have the new constitutions given above. The same result is attained by reducing the chlorocarbinols by a modification of Skita's process. Thus the chlorocarbinol of distyryl ketone in aqueous alcohol containing sodium methoxide, gum, and palladous chloride is reduced by hydrogen at 1·5 atmospheres to *$\alpha\epsilon$-diphenylpentan-α-ol*, $CH_2Ph\cdot[CH_2]_3\cdot CHPh\cdot OH$, b. p. 200—204°/20 mm., which yields $\alpha\epsilon$-diphenylpentan-α-one, m. p. 44—45°, by oxidation in acetic acid by potassium dichromate and sulphuric acid. This ketone, which has also been obtained by reducing cinnamylideneacetophenone in acetone by hydrogen and colloidal palladium in the presence of gum, has been obtained in two modifications; the stable form has m. p. 45—45·2°, and forms an oxime, m. p. 79—80·2°, whilst the labile form (only certainly isolated once) has m. p. 24·5—25·2°, and forms an oxime, m. p. 65·5—67° (compare Borsche, this vol., i, 194). The *keto-chloride* of cinnamylideneacetophenone (*$\alpha\epsilon$-dichloro-$\alpha\epsilon$-diphenyl-$\Delta^{\beta\delta}$-pentadiene*),

CHPhCl·CH:CH·CH:CPhCl,

m. p. 55—56°, forms a dark violet, crystalline *stannichloride*, dissolves in liquid sulphur dioxide with an intense violet colour, reacts with water and with methyl alcohol to form an oily *chlorocarbinol*, OH·CHPh·CH:CH·CH:CPhCl, and the corresponding *methyl ether* respectively, the latter being reconverted into the keto-chloride by hydrogen chloride.

It follows from the preceding results that the keto-chlorides and their chlorocarbinols and chloromethyl ethers are similarly constituted, and that their conversions into one another are cases of simple substitution.

Distyryl ketone can be converted into cinnamylideneacetophenone by the following series of reactions. The ketone is converted successively into its keto-chloride and the methyl ether of the corresponding chlorocarbinol, OMe·CHPh·CH:CCl·CH:CHPh. By boiling the last substance with 2% sodium methoxide in methyl alcohol for fifty to sixty hours, it is converted into the *acetal* of cinnamylideneacetophenone, $CPh(OMe)_2\cdot CH:CH\cdot CH:CHPh$, m. p. 60—60·5°, b. p. 216—218°/18—20 mm., from which cinnamylideneacetophenone is obtained by the addition of a little concentrated sulphuric acid to its methyl alcoholic solution. The same acetal is obtained from the keto-

chloride of cinnamylideneacetophenone by a similar series of reactions. The positions of the methoxy-groups are not indubitably proved by the oxidation of the acetal to phenylglyoxylic acid by potassium permanganate in acetone. The proof is furnished, however, by treating the acetal in methyl alcohol containing 5% sodium methoxide, gum, and palladous chloride with hydrogen under a pressure of 1·5 atmospheres, whereby the *acetal*, $CPh(OMe)_2\cdot[CH_2]_3\cdot CH_2Ph$, b. p. 194—197°/20 mm., of αε-diphenylpentan-α-one is produced, from which the diphenylpentanone, m. p. 44·5—45°, is obtained by hydrolysis.

In a similar manner di-*p*-chlorodistyryl ketone is converted into *di*-p *chlorocinnamylideneacetophenone*,

$$C_6H_4Cl\cdot CO\cdot CH\colon CH\cdot CH\colon CH\cdot C_6H_4Cl,$$

m. p. 162—162·5°, broad, yellow needles, which is also produced from p-*chlorocinnamaldehyde*, m. p. 62—62·5°, b. p. 155—156°/14 mm., and *p*-chloroacetophenone. The *acetal*,

$$C_6H_4Cl\cdot C(OMe)_2\cdot CH\colon CH\cdot CH\colon CH\cdot C_6H_4Cl,$$

b. p. about 198°/0 mm., cannot be conveniently purified. Also, dicinnamylideneacetophenone has been converted into *αι-diphenyl-$\Delta^{\beta\delta\zeta\theta}$-nonatetrene-α-one*, $COPh\cdot CH\colon CH\cdot CH\colon CH\cdot CH\colon CH\cdot CH\colon CHPh$, m. p. 126—126·5°, golden-yellow needles, which dissolves in concentrated sulphuric acid with a reddish-violet colour changing to brownish-violet, and forms an *acetal*, m. p. 115·5—116·5°.

With the object of obtaining a general method of preparing the non-halogenated, unsaturated alcohols corresponding with the preceding keto-chlorides and chlorocarbinols, di-*p*-chlorostyryl ketone has been converted successively into the following substances, the constitutions of most of which have been controlled by an examination of their products of oxidation. Di-*p*-chlorostyryl ketone is converted through the ketochloride into the methyl ether,

$$C_6H_4Cl\cdot CH(OMe)\cdot CH\colon CCl\cdot CH\colon CH\cdot C_6H_4Cl.$$

The latter is reduced by zinc dust and glacial acetic acid on the water-bath to *γ-chloro-αε-di-*p-*chlorophenyl-$\Delta^{\beta\delta}$-pentadiene*,

$$C_6H_4Cl\cdot CH_2\cdot CH\colon CCl\cdot CH\colon CH\cdot C_6H_4Cl,$$

m. p. 103—104°, colourless prisms or leaflets, which yields *p*-chlorobenzaldehyde, *p*-chlorobenzoic acid, and *p*-chlorophenylacetic acid by oxidation in acetone by potassium permanganate, and is converted into *α-methoxy-αε-di-*p-*chlorophenyl-$\Delta^{\beta\delta}$-pentadiene*,

$$C_6H_4Cl\cdot CH(OMe)\cdot CH\colon CH\cdot CH\colon CH\cdot C_6H_4Cl,$$

m. p. 79—79·5°, by boiling 0·5% methyl alcoholic sodium methoxide. The methoxy-compound dissolves in concentrated sulphuric acid with a reddish-blue colour and crimson fluorescence, which changes to yellowish-green and brownish-red fluorescence, and is oxidised in acetone by potassium permanganate to *p*-chlorobenzoic acid and *α-methoxy*-p-*chlorophenylacetic acid*, $C_6H_4Cl\cdot CH(OMe)\cdot CO_2H$, m. p. 85—86°. The latter acid has been prepared by converting *p*-chloromandelic acid into α-p-*dichlorophenylacetyl chloride*, $C_6H_4Cl\cdot CHCl\cdot COCl$, b. p. 129—132°/20 mm., by phosphorus pentachloride, and converting the latter into the required acid by boiling methyl alcoholic sodium methoxide and subsequent hydrolysis.

When a benzene solution of γ-chloro-αε-di-*p*-chlorophenyl-$\Delta^{\beta\delta}$-pentadiene is treated with sodium methoxide in the cold for twenty-four

hours and is occasionally warmed to 45—50°, α-methoxy-$\alpha\epsilon$-di-p-chlorophenyl-$\Delta^{\beta\delta}$-pentadiene is obtained, together with an *isomeride*, probably $C_6H_4Cl\cdot CH\colon CH\cdot CH(OMe)\cdot CH\colon CH\cdot C_6H_4Cl$, m. p. 108—108·5°, white leaflets.

γ-Chloro-$\alpha\epsilon$-di-p-chlorophenyl-$\Delta^{\beta\delta}$-pentadiene in boiling aqueous acetone is converted by 4% sodium hydroxide into *$\alpha\epsilon$-di-*p*-chlorophenyl-$\Delta^{\beta\delta}$-pentadien-α-ol*, $C_6H_4Cl\cdot CH(OH)\cdot CH\colon CH\cdot CH\colon CH\cdot C_6H_4Cl$, m. p. 111—112°, stout, white prisms, which yields the methyl ether, m. p. 79—79·5°, by treatment with boiling methyl alcohol containing two drops of concentrated hydrochloric acid. By treating this methyl ether or the isomeride, m. p. 108—108·5°, with phosphorus pentachloride in benzene, or the di-p-chlorophenylpentadienol itself in benzene with hydrogen chloride and calcium chloride, *α-chloro-$\alpha\epsilon$-di-*p*-chlorophenyl-$\Delta^{\beta\delta}$-pentadiene*, $C_6H_4Cl\cdot CHCl\cdot CH\colon CH\cdot CH\colon CH\cdot C_6H_4Cl$, m. p. 88—89°, yellow, round crystals, is obtained. This substance forms a dark-coloured *stannichloride* and *mercurichloride*,

$$C_{17}H_{13}Cl_3,3HgCl_2,$$

regenerates the pentadienol or its methyl ether by treatment with water or methyl alcohol, and forms an ozonide, by the decomposition of which by water, p-chlorobenzoic acid, p-chlorobenzaldehyde, α-p-dichlorophenylacetic acid (isolated as p-chloromandelic acid), and α-p-dichlorophenylacetaldehyde (isolated as p-chlorobenzoylcarbinol) are produced. p-*Chlorobenzoylcarbinol*, $C_6H_4Cl\cdot CO\cdot CH_2\cdot OH$, m. p. 122—123°, with sublimation, is obtained by boiling p-chloro-ω-bromoacetophenone with acetic acid and sodium acetate, and hydrolysing the resulting *acetate*, m. p. 65·5—66·5°, b. p. 174—175°/20 mm., broad leaflets, by boiling water and barium carbonate. By reduction with zinc dust and boiling glacial acetic acid, α-methoxy-$\alpha\epsilon$-di-p-chlorophenyl-$\Delta^{\beta\delta}$-pentadiene yields *$\alpha\epsilon$-di-*p*-chlorophenyl-$\Delta^{\beta\delta}$-pentadiene*,

$$C_6H_4Cl\cdot CH_2\cdot CH\colon CH\cdot CH\colon CH\cdot C_6H_4Cl,$$

m. p. 67—68°, broad needles, which does not react smoothly with bromine; the hydrogen atoms of the methylene group are not reactive, since the substance does not condense with diazobenzenesulphonic acid, and produces only a brown coloration with alcoholic potassium hydroxide and m-dinitrobenzene (under these conditions, fluorene produces an intense reddish-violet coloration).

The chlorobromides of the preceding unsaturated ketones, obtained by the action of hydrogen bromide on the chlorocarbinols (Abstr., 1910, i, 119, 565), are, in accordance with the views developed above, formulated as, for example, $CPhCl\colon CH\cdot CHBrPh$. The fact previously noted that the chlorobromides yield a mixture of the halogen hydrides and of the halogenated carbinols or their methyl ethers by treatment with water or methyl alcohol is explained by assuming that the chlorobromides are tautomeric:

$$CPhCl\colon CH\cdot CHPhBr \rightleftarrows CHPhCl\cdot CH\colon CPhBr,$$

although this explanation is attended by certain difficulties which have not been overcome.

[With W. HEITZ.]—The formation of arylimines by the interaction of primary aromatic amines and the keto-chlorides of unsaturated ketones (Straus and Ackermann, Abstr., 1910, i, 241), which is directly explicable with the old formulation of the latter, must, in

view of their new constitutions, be regarded as the result of the following changes: $CRCl:CH\cdot CHRCl \rightarrow CRCl:CH\cdot CHR\cdot NHR' \rightarrow CHRCl\cdot CH_2\cdot CR:NR' \rightarrow CHR:CH\cdot CR:NR'$. Thus the keto-chloride of *p*-chlorophenyl *p*-chlorostyryl ketone,

$$C_6H_4Cl\cdot CHCl\cdot CH:CCl\cdot C_6H_4Cl,$$

and *p*-anisidine (3 mols.) in benzene yield, after keeping for forty-five hours in darkness, p-*anisylimino*-p-*chlorophenyl*-p-*chlorostyrylmethane*, $C_6H_4Cl\cdot CH:CH\cdot C(C_6H_4Cl):N\cdot C_6H_4\cdot OMe$, m. p. 173·5°, yellow crystals (a colourless isomeride has not been detected; compare Straus and Ackermann), which forms a *hydrochloride*, $C_{22}H_{17}ONCl_2,HCl$, m. p. 166° (decomp.), yellow flocks, and a *picrate*, m. p. 151—151·5° (decomp.), reddish-yellow needles, yields *p*-anisidine and *p*-chlorophenyl *p*-chlorostyryl ketone by treatment with acetic and concentrated hydrochloric acids, and forms an additive *compound*,

$$C_6H_4Cl\cdot C(:N\cdot C_6H_4\cdot OMe)\cdot CH_2\cdot CH(C_6H_4Cl)\cdot NH\cdot C_6H_4\cdot OMe,$$

m. p. 122·5°, colourless leaflets, with *p*-anisidine in boiling benzene. A similar *compound*,

$$C_6H_4Cl\cdot C(:N\cdot C_6H_4Me)\cdot CH_2\cdot CH(C_6H_4Cl)\cdot NH\cdot C_6H_4Me,$$

m. p. 124·5—125·5°, glistening leaflets, is obtained from *p*-toluidine and Straus and Ackermann's yellow *p*-tolylimino-*p*-chlorophenyl-*p*-chlorostyrylmethane (not from the colourless isomeride) in boiling benzene. In boiling benzene, *p*-toluidine and *p*-anisylimino-*p*-chlorophenyl-*p*-chlorostyrylmethane or *p*-anisidine and yellow *p*-tolylimino-*p*-chlorophenyl-*p*-chlorostyrylmethane yield the same additive *cimpound*, $C_6H_4Cl\cdot C(:N\cdot C_6H_4\cdot OMe)\cdot CH_2\cdot CH(C_6H_4Cl)\cdot NH\cdot C_6H_4Me$ or

$$C_6H_4Cl\cdot C(:N\cdot C_6H_4Me)\cdot CH_2\cdot CH(C_6H_4Cl)\cdot NH\cdot C_6H_4\cdot OMe,$$

m. p. 127—128°, glistening leaflets. C. S.

Studies in the *cyclo*Pentadiene Series. I. 5-Nitro-2:3-diacetyl*cyclo*pentadiene. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1912, **34**, 1580—1590).—It has already been shown (this vol., i, 566) that acetonylacetone condenses with nitromalonaldehyde in presence of sodium hydroxide to form 5-nitro-2 : 3-diacetyl*cyclo*pentadiene, $NO_2\cdot C_5H_3Ac_2$. An account is now given of the *sodium*, *potassium*, and *barium* salts and certain derivatives of this compound. The *oxime*, m. p. 155° (decomp.), crystallises in lustrous, orange-yellow leaflets. The dioxime could not be obtained. The *anil*, m. p. 166·5°, forms clusters of yellow needles. The *phenylhydrazone*, m. p. 175—180° (decomp.), crystallises in slender, yellow needles, and the *hydrazone*, m. p. 185—190° (decomp.), forms small nodules.

By the action of benzaldehyde (4 mols.) on the sodium salt of 5-nitro-2 : 3-diacetyl*cyclo*pentadiene (1 mol.) in presence of excess of sodium hydroxide, the *sodium* salt of 5-nitro-2 : 3-dicinnamoyl*cyclo*pentadiene is produced, which is converted by acetic acid into 5-*nitro*-2 : 3-*dicinnamoyl*cyclo*pentadiene*, $NO_2\cdot C_5H_3(CO\cdot CH:CHPh)_2$, m. p. 253—255° (decomp.), which forms small, orange-yellow needles.

When 5-nitro-2 : 3-diacetyl*cyclo*pentadiene (1 mol.) is oxidised with potassium permanganate in presence of excess of potassium hydroxide, there are formed as potassium salts, acetic acid (2 mols.), oxalic acid (1 mol.), and carbonic acid (3 mols.). It is shown that this result affords good evidence of the structure of the *cyclo*pentadiene. The

compound does not combine with bromine, hydrogen bromide, or hydrogen iodide. E. G.

Some Derivatives of Acetophenoneacetone. CESARE FINZI (*Gazzetta*, 1912, **42**, ii, 356—363).—The author has established the constitution of the monoxime of this substance (Paal, Abstr., 1884, i, 599), for when treated with benzenesulphonyl chloride (compare Werner and Piguet, Abstr., 1905, i, 66) it yields carbylamine and a substance, $C_{17}H_{17}O_4NS$, which crystallises in colourless needles, m. p. 74°. This substance yields phenylcarbylamine when boiled with alcoholic potassium hydroxide, and the residue gives phenol when fused with alkali. In consequence of these reactions, the author ascribes to it the formula $\begin{array}{c}SO_2Ph\cdot O\cdot C\cdot CH_2\cdot CH_2\cdot COMe\\ \quad\quad\quad\quad\| \\ \quad\quad\quad PhN\end{array}$, the original oxime being therefore the *cis*oxime, $\begin{array}{c}Ph\cdot C\cdot CH_2\cdot CH_2\cdot COMe\\ \| \\ HO\cdot N\end{array}$.

Acetophenoneacetonemonosemicarbazone, $C_{12}H_{15}O_2N_3$, has m. p. 191°. In some preparations of the semicarbazone, another *substance*, m. p. 255—256°, was obtained. Acetic acid appears to convert the semicarbazone into a substance of the same composition, but of m. p. 210°. R. V. S.

Dioximes of Benzil. W. E. GARNER (*Chem. News*, 1912, **106**, 202).—The usual method of formulation of the three dioximes of benzil does not readily account for the fact that the γ-oxime loses water more readily than the α-oxime with formation of diphenylfurazan, but it is shown that if the two hydroxyl groups lie outside the plane of the remainder of the molecule these difficulties are removed. G. S.

Preparation of Dihalogenated Nitroanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249721. Compare Abstr., 1903, i, 498).—1 : 5-*Dichloro-4-nitroanthraquinone*, yellow needles, is prepared by dissolving 1 : 5-dichloroanthraquinone (20 parts) in 400 parts of fuming sulphuric acid, and adding nitric acid (20%) at a temperature of 40—50°. When 1 : 8-dichloroanthraquinone dissolved in concentrated sulphuric acid at 20° is treated with an excess of nitric acid (2 mols.), it furnishes 1 : 8-*dichloro-4-nitroanthraquinone*, yellow prisms; whilst 1 : 5-*dibromo-4-nitroanthraquinone*, yellow needles, is obtained in a similar manner. F. M. G. M.

Preparation of Arylaminoanthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 248655).—Numerous condensation products from aminoanthraquinones and halogenated compounds have been prepared previously; the reaction has now been extended to compounds of the general formula: $Z\cdot C_6H_4\cdot X\cdot C_6H_4Z$ and $Z\cdot C_6H_3{<}^{Y}_{Y}{>}C_6H_3Z$ (where X is oxygen, sulphur, or an imino-group, Y a radicle with two free valencies, such as CO or NH, and Z a halogen atom), which condense with two molecules of α-aminoanthraquinone; and the preparation of *compounds* from this base with dibromodiphenyl ether, *pp*-dichlorodiphenyl sulphide, *pp*-dibromodiphenylamine, and

with 2 : 7-dibromoxanthone are described in the original; they form red or reddish-brown crystals, and their solutions in different solvents exhibit marked colour reactions. F. M. G. M.

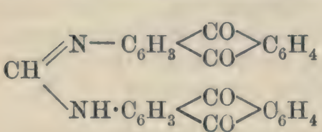
[Preparation of Anthraquinone Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248997).—Condensation products of halogenated anthraquinones with aminoanthraquinones have previously been prepared; this reaction has now been extended to ω-chloroacetylaminoanthraquinones, and yields compounds (in their most simple form) of the type $NHX·CO·CH_2·NHX$ (X = anthraquinone).

The *compound* from 2-aminoanthraquinone and ω-chloroacetyl-2-aminoanthraquinone forms orange crystals; its tinctorial properties with those of other analogous compounds are tabulated in the original.

F. M. G. M.

[Preparation of Anthracene Derivatives.] FRITZ ULLMANN (D.R.-P. 248999. Compare Abstr., 1907, i, 224).—When the *compound*, m. p. 188° (obtained from benzaldehyde and 1 : 3-dibromo-2-aminoanthraquinone), is heated at 200—240° in the presence of copper powder, it furnishes a *dibromodiaminodianthraquinonyl*, a pale yellow, crystalline powder, m. p. 290°. F. M. G. M.

Preparation of Condensation Products in the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248656. Compare this vol., i, 811).—The *amidine* (annexed formula) is obtained when 2-aminoanthraquinone is heated at 130—140° with ethyl orthoformate.



Benzoyl-2-anthraquinonylimide chloride is prepared by the action of phosphorus pentachloride on benzoyl-2-aminoanthraquinone, and this when condensed with 2-aminoanthraquinone furnishes the *amidine*, $C_6H_5·C{<}{}^{N—C_{14}H_7O_2}_{NH·C_{14}H_7O_2}$, yellow needles, m. p. 334—335°, which can also be obtained by heating together 2-aminoanthraquinone, benzotrichloride, and nitrobenzene at 150—160° during several hours.

F. M. G. M.

Preparation of Hydroxyanthrimides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 249938. Compare Abstr., 1909, i, 242).—*Hydroxy*-1 : 1′-*dianthrimide*, $OH·C_{14}H_6O_2·NH·C_{14}H_7O_2$, dark violet needles, is obtained when 1 : 1′-dianthrimide is heated at 170° with concentrated sulphuric acid, sodium nitrite, and boric acid, whilst *hydroxy*-1 : 5-*trianthrimide*, glistening, violet leaflets (from nitrobenzene), is obtained in a similar manner from 1 : 5-trianthrimide.

F. M. G. M.

Derivatives of Anthraquinone. WOLFGANG LENHARD (*Zeitsch. angew. Chem.*, 1912, 25, 2152—2155).—1-*Amino-2-thiolanthraquinone*, prepared from 2-bromo-1-aminoanthraquinone by the action of alcoholic sodium sulphide, gives rise to a *disulphide*, *esters*, and *ethers*, which

may be converted into the corresponding *acetyl* and *benzoyl* derivatives; the *phenyl* and *tolyl* ethers are obtained by heating 2-bromo-1-amino-anthraquinone with phenyl and tolyl mercaptans in an alkaline alcoholic solution. The *sodium* salt of 1-amino-2-thiolanthraquinone reacts with ethylene dibromide to form the *di*-1-*amino*-2-*anthraquinonyl ether* of *dithioethylene glycol*, and with *s*-dichloroethane, yielding the corresponding *ether* of *dithiolacetylene* (? *dithiolethylene*); with cyanogen iodide it forms 1-*amino*-2-*anthraquinonyl thiocyanate.*

Attempts to replace the amino-group of 2-bromo-1-aminoanthraquinone by the thiol group were unsuccessful; the amino-compound readily diazotises and yields a crystalline *diazonium thiocyanate*, which, however, is transformed by boiling with water into a mixture of 2-*bromo*-1-*anthraquinonyl thiocyanate* and 1 : 2-*dithiocyanoanthraquinone.*

Ethers of *dithioalizarin* (1 : 2-*dithiolanthraquinone*) have been prepared from the above-mentioned 1-amino-2-thiolanthraquinone ethers by introducing the thiocyano-group in the 1-position, followed by hydrolysis and treatment with alkyl haloids; in this manner, the *dimethyl*, *methylethyl*, *diethyl*, and *methylbenzyl ethers* were obtained.

The sodium salt of 1-amino-2-thiolanthraquinone, and also the methyl, ethyl, and benzyl ethers, react with benzoyl chloride, yielding a *thiazole*; with ethyl chlorocarbonate the sodium salt forms an *ethyl thiocarbonate*, which, by the action of glacial acetic acid or alcoholic potassium hydroxide, is converted into a *ketohydrothiazole* or a *hydroxyl thiazole*. With ethyl chloroacetate it gives rise to an *ethyl thiolacetate*, from which a *dihydrothiazine* of anthraquinone is produced by boiling with acetic acid.

Thiazole derivatives containing a thiol group in the thiazole ring have hitherto not been prepared in the anthraquinone series; a *thiazole* of this kind has now been obtained by heating the sodium salt of 1-amino-2-thiolanthraquinone with carbon disulphide; on treatment with alcoholic potassium hydroxide and alkyl haloids, it yields the corresponding ethers.

1-Amino-2-thiolanthraquinone condenses with acetone (1 mol.) to form a *dimethylthiazole.*

In attempting to prepare di-1-thiocyanoanthraquinonyl 2-disulphide from *di*-1-*aminoanthraquinonyl* 2-*disulphide* by means of the diazo-reaction, *anthraquinone*-1 : 2-*diazosulphide* was obtained.

When heated at 200°, di-1-aminoanthraquinonyl 2-disulphide is transformed into the *monosulphide* (*di*-1-*aminoanthraquinonyl* 2-*sulphide*), m. p. above 350°, which has also been prepared by heating 2-bromo-1-aminoanthraquinone with the sodium salt of 1-amino-2-thiolanthraquinone.

The sodium salt just-mentioned reacts with *s*-tetrabromoethane in the presence of sodium sulphide, yielding *di*-1-*aminoanthraquinonyl* 2-*trisulphide*, slender, red needles, m. p. 262°; attempts to prepare trisulphides from the sodium salts of 1-thiol-, 2-thiol-, and 1-amino-2 : 4-dithiol-anthraquinones by the same method were unsuccessful.

The above trisulphide is also obtained by crystallising di-1-amino-anthraquinonyl 2-disulphide from pyridine.

With the object of determining whether the transformation of

disulphides is accompanied by the liberation of sulphur in the free condition as suggested by Beilstein, or to the simultaneous formation of a trisulphide, as was found by Hinsberg in the benzene and naphthalene series, the author has examined the behaviour of a number of disulphides, and finds that the simple 1- and 2-disulphides when heated are quite stable, whilst the 1-amino-derivatives of the disulphides and 2 : 4-disulphides lose an atom of sulphur and give rise to monosulphides; in no case was a trisulphide obtained. From these results the conclusion is drawn that the formation of monosulphides in the anthraquinone series takes place in the manner suggested by Beilstein, and is restricted to those compounds having the disulphide group in the 2-position.

Replacement of the halogens in 2 : 4-dibromo-1-aminoanthraquinone by the thiol group yields 1-*amino*-2 : 4-*dithiolanthraquinone*. This gives rise to *methyl*, *ethyl*, and *benzyl ethers*, and reacts with ethylene dibromide (1 mol.) to form an *ether* of *dithioethylene glycol*. It is oxidised by potassium ferricyanide to a *bidisulphide*, which, on crystallisation from pyridine, loses sulphur and is converted into a *monodisulphide*.

2 : 4-Dibromo-1-aminoanthraquinone reacts with oxalyl chloride in ethereal solution, yielding 2 : 4-*dibromo*-1-*anthraquinonyloximide*,

$$C_{14}H_{15}O_2Br \cdot N<\begin{matrix}CO\\|\\CO\end{matrix};$$

in carbon tetrachloride solution at 130°, the *compound*,

$$C_{14}H_5O_2Br \cdot N<\begin{matrix}CO\\CO\end{matrix}>N \cdot C_{15}H_5O_2Br,$$

is produced. F. B.

Mercaptans of Anthraquinone. Ludwig Gattermann (*Annalen*, 1912, 393, 113—197).—Since by the action of sodium alkyloxides, 1-nitroanthraquinone is converted into 1-alkyloxyanthraquinones, the author hoped to obtain 1-thiolanthraquinone from 1-nitroanthraquinone by the action of potassium hydrosulphide; the substance produced, however, is 1-aminoanthraquinone. The action of potassium aryl mercaptides on 1-nitroanthraquinone yields 1-anthraquinonyl aryl sulphides, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3 \cdot SAr$, from which the aryl group cannot be removed even by aluminium chloride.

1-Thiolanthraquinone can be obtained by diazotising 1-aminoanthraquinone in sulphuric acid, boiling the diazonium sulphate with aqueous potassium thiocyanate, and boiling the resulting 1-thiocyanoanthraquinone with 10% alcoholic potassium hydroxide, whereby the potassium salt of thet hiolanthraquinone is produced. Substituted 1-aminoanthraquinones undergo similar changes.

The sulphate of the aminoanthraquinone is diazotised in the usual manner, but when an aminoanthraquinone which does not form a sulphate in dilute sulphuric acid is used, its solution in concentrated sulphuric acid is diazotised at the ordinary temperature by nitrososulphuric acid. In either case, the solution is diluted with water or ice, treated with an excess of 20% aqueous potassium thiocyanate in the cold (whereby a crystalline diazonium thiocyanate occasionally is

precipitated), and the mixture is heated on the water-bath and finally over a naked flame until the evolution of nitrogen ceases and the precipitated thiocyanoanthraquinone has coagulated.

After the thiocyanoanthraquinone has been boiled with 10% alcoholic potassium hydroxide until a clear solution has been obtained, an equal volume of water is added and the solution is ready for the numerous transformations of the thiolanthraquinones mentioned below. By acidification the solution yields the free thiolanthraquinone, which, however, changes very readily to the disulphide.

The thiocyanoanthraquinones all crystallise extremely easily, and are yellow or yellowish-brown if hydroxyl or basic groups are not present; those containing hydroxyl or basic groups are orange or reddish-violet to violet respectively.

1-*Thiocyanoanthraquinone*, $C_6H_4<\substack{CO\\CO}>C_6H_3\cdot SCN$, m. p. 241°, crystallises in yellow needles. The dark violet, alkaline solution of 1-thiolanthraquinone obtained by its decomposition as above yields the *disulphide*, $C_{28}H_{14}O_4S_2$, m. p. above 350°, yellow, rhombic plates, quantitatively by oxidation with aqueous potassium ferricyanide, and reacts with methyl iodide to form 1-*methylthiolanthraquinone*, $C_6H_4<\substack{CO\\CO}>C_6H_3\cdot SMe$, m. p. 208°, yellow needles. The corresponding 1-*ethylthiol*, m. p. 183°, crystallises in yellow prisms; the 1-*benzylthiol*, m. p. 241°, in golden-yellow needles, and the *ethylenethiol*, $C_{14}H_7O_2\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot C_{14}H_7O_2$ (from ethylene dibromide), m. p. above 350°, in canary-yellow needles. By oxidation with chromic and acetic acids, these four ethers are oxidised to the respective *sulphones*, m. p. 251°, 210°, 231°, and 185°. 1-Thiolanthraquinone forms a *benzoyl* derivative, m. p. 207°, yellow needles.

2-*Thiocyanoanthraquinone*, m. p. 205°, crystallises in golden-yellow needles. 2-*Thiolanthraquinone*, m. p. 206°, stout, yellow needles, obtained as above or by heating 2-chloroanthraquinone with sodium sulphide under pressure, yields the following derivatives: *disulphide*, m. p. 257°, pale yellow needles; *methyl thio-ether*, m. p. 162°, yellow needles (*sulphone*, m. p. 230°, yellow prisms); *ethyl thio-ether*, m. p. 138°, golden needles (*sulphone*, m. p. 154°, pale yellow prisms); *benzyl thio-ether*, m. p. 138°, golden-yellow needles (*sulphone*, m. p. 212°, yellow prisms); *ethylene thio-ether*, $C_{30}H_{18}O_4S_2$, m. p. 302°, yellow needles; *allyl thio-ether*, m. p. 126°, yellow needles (*sulphone*, m. p. 159°, pale yellow needles), and *benzoyl* derivative, m. p. 180°, small, yellow needles.

1-*Thiocyano-2-methylanthraquinone*, m. p. 193—194°, pale yellow needles, is obtained from 1-amino-2-methylanthraquinone. From the alkaline solution of 1-thiol-2-methylanthraquinone have been prepared the *disulphide*, m. p. 247°, yellow needles; *methyl thio-ether*, m. p. 124°, orange-red needles (*sulphone*, m. p. 198°, yellowish-red plates); *ethyl thio-ether*, m. p. 99°, orange-red leaflets; and *benzyl thio-ether*, m. p. 139°, orange-red needles.

1-*Thiocyano-4-methoxyanthraquinone*, m. p. 245°, yellow needles, is obtained from 1-amino-4-methoxyanthraquinone. The corresponding mercaptan yields a *disulphide*, m. p. 282—283°, red needles; *benzyl*

thio-ether, m. p. 200°, dark red leaflets (*sulphone*, m. p. 197°, pale red prisms), and *ethyl thio-ether*, m. p. 148°, red needles.

1-*Thiocyano-4-aminoanthraquinone*, m. p. 256°, reddish-violet needles, is obtained from 1 : 4-diaminoanthraquinone. Its *acetyl* derivative, $C_{17}H_{10}O_3N_2S$, m. p. 263°, crystallises in red needles. 4-Amino-1-thiolanthraquinone forms a *disulphide*, m. p. above 300°, violet needles; *methyl thio-ether*, m. p. 200° (decomp.), violet-red needles (*acetyl* derivative, m. p. 226° [decomp.], red needles); *benzyl thio-ether*, m. p. 225°, violet needles (*sulphone*, m. p. 264°, brownish-yellow needles, by oxidation with 15% hydrogen peroxide), and *allyl thio-ether*, m. p. 175°, reddish-violet needles.

1-*Thiocyano-4-methylaminoanthraquinone*, m. p. 242—243°, dark violet needles, is obtained from 1-amino-4-methylaminoanthraquinone (*diacetyl* derivative, $C_{19}H_{16}O_4N_2$, m. p. 278°). 4-Methylamino-1-thiolanthraquinone forms a *disulphide*, m. p. 280°, dark violet needles, and *methyl thio-ether*, m. p. 210°, violet needles.

1-*Thiocyano-4-dimethylaminoanthraquinone*, m. p. 241°, crystallises in Bordeaux-red needles. The corresponding mercaptan yields a *disulphide*, m. p. 220° (decomp.), bluish-violet crystals, and *methyl thio-ether*, m. p. 247°, violet needles, the *sulphone* of which, m. p. 193°, forms reddish-brown needles.

1-*Thiocyano-4-hydroxyanthraquinone*, m. p. 231°, brownish-red needles, is obtained from 1-amino-4-hydroxyanthraquinone. The corresponding mercaptan yields a *disulphide*, m. p. above 300°, reddish-brown needles; *methyl thio-ether*, m. p. 194°, reddish-brown needles, and *benzyl thio-ether*, m. p. 242°, bluish-red needles (*sulphone*, m. p. 216°, yellow needles).

1-*Thiocyano-3 : 4-dihydroxyanthraquinone*, m. p. above 350°, obtained from 4-aminoalizarin, crystallises in yellowish-red needles. The corresponding mercaptan forms a *disulphide*, m. p. above 300°, red needles, and *methyl thio-ether*, m. p. 248°, red needles.

1 : 4-*Dithiocyanoanthraquinone*, m. p. above 300°, yellow needles, is obtained directly by boiling diazotised 4-nitro-1-aminoanthraquinone or 4-chloro-1-aminoanthraquinone with aqueous potassium thiocyanate. The corresponding dimercaptan forms a *dimethyl thio-ether*, m. p. 127°, reddish-brown needles (*disulphone*, m. p. 280°, pale yellow needles); *diethyl thio-ether*, m. p. 117°, reddish-yellow needles (*disulphone*, m. p. 217°, yellow needles), and *dibenzyl thio-ether*, m. p. 230°, red leaflets (*disulphone*, m. p. 263°, yellow needles). 1-*Iodo-4-nitroanthraquinone*, m. p. 259°, yellow needles, is obtained by boiling diazotised 4-nitro-1-aminoanthraquinone with aqueous potassium iodide.

1 : 5-*Dithiocyanoanthraquinone*, m. p. above 350°, yellow needles, yields the dimercaptan, the *diethyl thio-ether* of which has m. p. 230°, and crystallises in red needles.

1-*Thiocyano-5-aminoanthraquinone*, m. p. 235°, dark red crystals, is obtained from 1 : 5-diaminoanthraquinone. It yields 5-amino-1-thiolanthraquinone, the *benzyl thio-ether* of which crystallises from pyridine in green metallic needles, m. p. 196°, containing $2C_5NH_5$.

5-*Chloro-1-aminoanthraquinone*, m. p. 210°, dark red needles (*acetyl* derivative, m. p. 216°, yellow leaflets), yields 5-*chloro-1-thiocyanoanthraquinone*, m. p. 287°, golden-yellow needles; the mercaptan forms

a *disulphide*, m. p. above 360°, yellowish-brown needles, and *methyl thio-ether*, m. p. 228°, brownish-red needles.

1-*Thiocyano*-5-*methylaminoanthraquinone*, m. p. 268°, dark reddish-violet needles, yields a mercaptan, the *disulphide* of which, red crystals, has m. p. 321°, and the *methyl thio-ether*, tufts of dark red needles, has m. p. 248°.

1-*Thiocyano*-5-*dimethylaminoanthraquinone*, m. p. 212°, reddish-violet needles, yields a mercaptan which forms a *disulphide*, m. p. 272°, red needles, and *methyl thio-ether*, m. p. 176·5°, red needles.

5-*Piperidyl*-1-*aminoanthraquinone*, $C_5NH_{10}\cdot C_6H_3<\substack{CO\\CO}>C_6H_3\cdot NH_2$, m. p. 149°, brownish-red plates, yields 1-*thiocyano*-5-*piperidylanthraquinone*, m. p. 164°, violet needles; the mercaptan forms a *benzyl-thio-ether*, m. p. 210°, almost black needles.

8-*Piperidyl*-1-*aminoanthraquinone*, m. p. 180°, dark violet crystals, yields 1-*thiocyano*-8-*piperidylanthraquinone*, m. p. 164°, dark violet needles; the mercaptan forms a *methyl thio-ether*, m. p. 187°, brownish-red needles.

1 : 8-*Dithiocyanoanthraquinone*, m. p. above 300°, yellow needles, yields 1 : 8-dithiolanthraquinone, which forms a *dimethyl thio-ether*, m. p. 221°, brownish-red needles; *diethyl thio-ether*, m. p. 169°, red needles, and *dibenzyl thio-ether*, m. p. 240°, orange-red needles.

1 : 4-Diaminoanthraquinone is diazotised by 1 mol. of nitrous acid, and an aqueous paste of the resulting sulphate is heated with cuprous cyanide. By hydrolysing the product with 10% sodium carbonate at 150° and acidifying, 1-*aminoanthraquinone*-4-*carboxylic acid*, m. p. 246—248° (decomp.), dark brown needles, is obtained. It yields 1-*thiocyanoanthraquinone*-4-*carboxylic acid*, decomp. 280°, greyish-yellow needles; the *methyl thio-ether*, m. p. 278°, of the corresponding mercaptan crystallises in yellowish-red needles.

1-*Amino*-5-*cyanoanthraquinone*, m. p. 300°, dark red leaflets, yields 1-*aminoanthraquinone*-5-*carboxylic acid*, m. p. 265°, red prisms, by hydrolysis, from which 1-*thiocyanoanthraquinone*-5-*carboxylic acid*, m. p. 307°, yellowish-brown needles, is obtained; the corresponding mercaptan forms a *methyl thio-ether*, m. p. 276°; yellowish-brown needles.

1-*Aminoanthraquinone*-5-*sulphonic acid* is obtained by reducing 1-nitroanthraquinone-5-sulphonic acid with aqueous sodium sulphide; its *potassium* salt crystallises in reddish-violet prisms containing H_2O. 1-*Thiocyanoanthraquinone*-5-*sulphonic acid* forms a *potassium* salt, $C_{15}H_6O_5NS_2K,H_2O$, yellowish-brown leaflets. The corresponding mercaptan forms a *disulphide*, $C_{28}H_{12}O_{10}S_4K_2$, yellow needles or large, red prisms, and *methyl thio-ether*, $C_{15}H_9O_5S_2K,2H_2O$, orange-red crystals.

1-*Aminoanthraquinone*-8-*sulphonic acid* forms a *potassium* salt, red prisms. *Potassium* 1-*thiocyanoanthraquinone*-8-*sulphonate*,

$$C_{15}H_6O_5NS_2K,1\tfrac{1}{2}H_2O,$$

brown prisms, yields a mercaptan which does not form a disulphide, and the *methyl thio-ether*, $C_{15}H_9O_5S_2K$, of which crystallises in orange-red needles.

Potassium 1-*aminoanthraquinone*-6-*sulphonate*, $C_{14}H_8O_5NSK,3\tfrac{1}{2}H_2O$, red prisms, yields *potassium* 1-*thiocyanoanthraquinone*-6-*sulphonate*,

$C_{15}H_6O_5NS_2K,H_2O$, yellow needles; the corresponding mercaptan forms a *disulphide*, $C_{28}H_{12}O_{10}S_4K_2$, yellow prisms, and *methyl thio-ether*, $C_{15}H_9O_5S_2K,2H_2O$, orange-red prisms.

1-*Aminoanthraquinone*-7-*sulphonic acid*, violet-red, stellate needles, yields 1-*thiocyanoanthraquinone*-7-*sulphonic acid*, the *potassium* salt of which, $C_{15}H_6O_5NS_2K,H_2O$, pale yellow, rectangular prisms, forms a mercaptan, of which the *disulphide*, $C_{28}H_{12}O_{10}S_4K_2,5H_2O$, pale yellow plates, and *methyl thio-ether*, $C_{15}H_9O_5S_2K$, orange-red needles, are mentioned.

In solution, the alkali salts of the preceding mercaptans exhibit colours which are nearer the blue end of the spectrum than those of the alkali salts of the corresponding hydroxyanthraquinones.

Anthraquinonyl aryl sulphides are obtained from nitroanthraquinones and potassium aryl mercaptides in boiling alcohol. Thus 1-nitroanthraquinone yields 1-*phenylthiolanthraquinone*,

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_3{\cdot}SPh,$$

m. p. 185°, yellowish-red needles, and the corresponding 1-o-*tolylthiol* derivative, m. p. 216°, reddish-brown needles, and p-*tolylthiol* compound, m. p. 235°, orange-red needles; 1 : 5-dinitroanthraquinone yields 1 : 5-*diphenylthiolanthraquinone*, $SPh{\cdot}C_6H_3{<}^{CO}_{CO}{>}C_6H_3{\cdot}SPh$, m. p. 250°, reddish-brown leaflets, and the corresponding *di*-p-*tolylthiol* compound, m. p. above 300°, golden-yellow needles. The following are obtained in a similar manner: *potassium* 1-*phenylthiolanthraquinone*-5-*sulphonate*, $C_{20}H_{11}O_5S_2K$, yellowish-red needles, and the corresponding p-*tolyl* derivative, $C_{21}H_{13}O_5S_2K$, golden-yellow needles; *benzyl* derivative, $C_{21}H_{13}O_5S_2K,2H_2O$, golden-yellow needles; *salicyl* derivative, $C_{21}H_{11}O_7S_2K$, orange-red leaflets; p-*nitrophenyl* derivative, $C_{20}H_{10}O_7NS_2K$, yellow needles; p-*aminophenyl* derivative, $C_{20}H_{12}O_5NS_2K$, brown needles (by reduction of the preceding compound by alcoholic sodium sulphide); *potassium* 1-*phenylthiolanthraquinone*-8-*sulphonate*, $C_{20}H_{11}O_5S_2K$, orange needles, and the corresponding p-*tolyl* derivative, $C_{21}H_{13}O_5S_2K$, brick-red needles; *potassium* 1-*ethylthiolanthraquinone*-6-*sulphonate*, $C_{16}H_{11}O_5S_2K$, yellow leaflets, and the corresponding *phenyl* derivative, $C_{20}H_{11}O_5S_2K$, yellow needles; p-*tolyl* derivative, $C_{21}H_{13}O_5S_2K$, yellow needles; *salicyl* derivative, $C_{21}H_{11}O_7S_2K$, yellow leaflets; 1-*amino*-4-*phenylthiolanthraquinone*, $C_{20}H_{13}O_2NS$, m. p. 201°, bluish-red needles (*acetyl* derivative, m. p. 224°, reddish-brown needles); 1-*amino*-4-p-*tolylthiolanthraquinone*, m. p. 218°, bluish-red leaflets (*acetyl* derivative, m. p. 278°, reddish-brown needles); 1-*amino*-4-*salicylthiolanthraquinone*, as *potassium* salt, $C_{21}H_{12}O_4NSK$ (*ethyl* ester, m. p. 166°, bluish-red needles), and 1-*amino*-4-a-*naphthylthiolanthraquinone*, m. p. 232°, dark red needles.

1-*Thiocyano*-4-*phenylthiolanthraquinone*,

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_2(SCN){\cdot}SPh,$$

m. p. 228°, yellowish-red needles, obtained by boiling diazotised 1-amino-4-phenylthiolanthraquinone with aqueous potassium thiocyanate, is

converted by alcoholic potassium hydroxide and subsequent treatment with methyl iodide into 4-*phenylthiol*-1-*methylthiolanthraquinone*, m. p. 182°, red needles. 1-*Thiocyano*-4-p-*tolylthiolanthraquinone*, m. p. 241°, reddish-yellow needles, m. p. 241°, yields 4-p-*tolylthiol*-1-*methylthiolanthraquinone*, m. p. 215°, red leaflets; the *disulphide*, m. p. above 330°, of the mercaptan crystallises in orange-red needles.

New types of sulphur compounds, which can be isolated on account of their pronounced tendency to crystallise, have been obtained from the mercaptans of the anthraquinone series. Thus *anthraquinonylthiolacetic acid*, $C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CH_2\cdot CO_2H$, m. p. 250°, yellow needles, is obtained from 1-thiolanthraquinone and chloroacetic acid in boiling alkaline solution; it forms an *ethyl* ester, m. p. 148°, yellow needles, and a *sulphoxide*, m. p. 240, pale yellow needles, the *ethyl* ester of which has m. p. 144°. Also an aqueous alcoholic alkaline solution of 1-thiolanthraquinone by treatment with ethylene dibromide yields 1-β-*bromoethylthiolanthraquinone*, $C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CH_2\cdot CH_2Br$, m. p. 180°, yellow needles, from which 1-*vinylthiolanthraquinone*,

$$C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CH{:}CH_2,$$

m. p. 163°, brownish-red needles, is obtained by the action of boiling alcoholic potassium hydroxide. By the addition of bromine in cold chloroform, the vinyl compound yields 1-$\alpha\beta$-*dibromoethylthiolanthraquinone*, $C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CHBr\cdot CH_2Br$, m. p. 160°, golden-yellow needles, which is converted by boiling aqueous alcoholic potassium hydroxide into 1-*acetenylthiolanthraquinone*,

$$C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot C{:}CH,$$

m. p. 198—199°, golden-yellow needles or plates (*silver* derivative, red, slightly explosive powder).

1-β-*Acetoxyethylthiolanthraquinone*,

$$C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CH_2\cdot CH_2\cdot OAc,$$

m. p. 148°, yellow needles, obtained by heating the bromo-compound with acetic acid, acetic anhydride, and potassium acetate, is hydrolysed by aqueous potassium hydroxide, yielding 1-β-*hydroxyethylthiolanthraquinone*, $C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CH_2\cdot CH_2\cdot OH$, m. p. 178°, orange-red needles; the *benzoate*, m. p. 201°, crystallises in yellow needles. By heating with alcohol at 130°, 1-β-*bromoethylthiolanthraquinone* yields 1-β-*ethoxyethylthiolanthraquinone*,

$$C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CH_2\cdot CH_2\cdot OEt,$$

m. p. 129°, reddish-yellow needles.

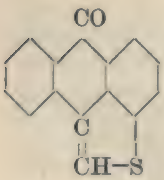
1-$\alpha\beta$-Dibromoethylthiolanthraquinone yields 1-$\alpha\beta$-*dimethoxyethylthiolanthraquinone*, $C_6H_4<\substack{CO\\CO}>C_6H_3\cdot S\cdot CH(OMe)\cdot CH_2\cdot OMe$, m. p. 156°, yellow needles, or the corresponding *diethoxy*-compound, m. p. 156°, by

heating with methyl or ethyl alcohol. By heating with alcoholic potassium hydroxide under suitable conditions, the dibromo-compound yields 1-*a*(or *β*)-*ethoxyvinylthiolanthraquinone*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3\cdot S\cdot C(OEt)\colon CH_2$$

or $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3\cdot S\cdot CH\colon CH\cdot OEt$, m. p. 197—198°, dark red leaflets; the corresponding *methoxy*-compound, m. p. 215°, crystallises in red needles. By boiling an aqueous methyl alcoholic alkaline solution of 1-thiolanthraquinone with *s*-dichloroethylene, 1-*β*-*chlorovinylthiolanthraquinone*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3\cdot S\cdot CH\colon CHCl$, m. p. 174—175°, red needles, and the preceding acetenyl derivative are produced. The *substance*, $C_2H_2(S\cdot C_{14}H_7O_2)_2$, m. p. 341°, dark red leaflets, can be obtained from alkaline 1-thiolanthraquinone and *s*-dichloroethylene under suitable conditions, or by heating 1-*aβ*-dibromoethylthiolanthraquinone with pyridine at 150°; in the latter method, methylene bromide must be eliminated.

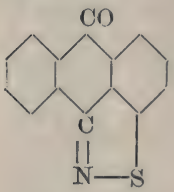
The following substances have been obtained by similar methods: 2-*anthraquinonylthiolacetic acid*, m. p. 202°, yellow needles (*methyl* ester, m. p. 131°; *ethyl* ester, m. p. 112°; *sulphoxide*, m. p. 247°, yellow prisms [*ethyl* ester, m. p. 215°]); 2-*β*-*bromoethylthiolanthraquinone*, m. p. 172°, pale yellow needles; 2-*vinylthiolanthraquinone*, m. p. 133°, golden-yellow needles; 2-*aβ*-*dibromoethylthiolanthraquinone*, m. p. 133·5°, yellow plates; 2-*β*-*hydroxyethylthiolanthraquinone*, m. p. 137° (*acetate*, m. p. 128°; *benzoate*, m. p. 128·5°; *ethyl ether*, m. p. 110°); 2-*aβ*-*diethoxyethylthiolanthraquinone*, m. p. 106°; 2-*acetenylthiolanthraquinone*, m. p. 323°, red leaflets; 4-*methoxyanthraquinonylthiolacetic acid*, m. p. 220°, pale red needles; 4-*aminoanthraquinonylthiolacetic acid*, m. p. 206° (decomp.), red needles; 4-*methylaminoanthraquinonylthiolacetic acid*, m. p. 232°, dark violet leaflets; 5-*chloroanthraquinonylthiolacetic acid*, m. p. 278°, pale yellow needles; 5-*dimethylamino*-1-*β*-*bromoethylthiolanthraquinone*, m. p. 186°, red leaflets; 5-*dimethylamino*-1-*vinylthiolanthraquinone*, m. p. 161·5°, reddish-brown leaflets; 5-*dimethylamino*-1-*aβ*-*dibromoethylthiolanthraquinone*, m. p. 143°, dark brown leaflets; 5-*dimethylamino-acetenylthiolanthraquinone*, m. p. 197°, reddish-brown prisms.



By heating with acetic anhydride under pressure, anthraquinonylthiolacetic acids are converted into anthraquino-1-thiophens. In some cases the tendency to ring closure is so pronounced that the thiophens are produced in the usual method of preparing the thiolacetic acids. *Anthraquino*-1-*thiophen*, m. p. 179—180° (annexed formula), crystallises in pale yellow needles. 2-*Methylanthraquino*-1-*thiophen*, $C_{16}H_{10}OS$, m. p. 186°, yellow needles, 2-*methylanthraquino*-1-*thiophencarboxylic acid*, m. p. 271°, citron-yellow needles, and 4-*methoxyanthraquino*-1-*thiophen*, m. p. 202—203°, yellowish-brown leaflets, are described.

By heating with concentrated aqueous ammonia at 130°, 1-thiocyanoanthraquinone is converted into *anthraquino*-1-*thiazole* (annexed

formula), m. p. 221°, yellow needles. The following thiazoles have also been prepared; 2-*methylanthraquino*-1-*thiazole*, m. p. 218°, pale yellow needles; 4-*aminoanthraquino*-1-*thiazole*, m. p. 251°, golden plates or needles; 4-*methylaminoanthraquino*-1-*thiazole*, m. p. 219°, greenish metallic leaflets; 4-*dimethylaminoanthraquino*-1-*thiazole*, m. p. 212°; *anthraquino*-1:4-*dithiazole*, m. p. 226°, citron-yellow needles; *anthraquino*-1-*thiazole*-4-*carboxylic acid*, m. p. 260°, yellow needles; 4-*tolylthiolanthraquino*-1-*triazole*, m. p. 210°, yellow leaflets; 5-*aminoanthraquino*-1-*thiazole*, m. p. 250°, reddish-brown needles with green reflex; 5-*thiocyanoanthraquino*-1-*thiazole*, m. p. 276°, golden needles; 5-*methylthiolanthraquino*-1-*thiazole*, m. p. 245°, orange needles; 5-*methylaminoanthraquino*-1-*thiazole*, m. p. 185°, reddish-violet needles; 5-*dimethylaminoanthraquino*-1-*thiazole*, m. p. 152°, brownish-red needles, and *anthraquino*-1:5-*dithiazole*, m. p. 287°, yellow needles.



The dyeing properties of many of the preceding substances are described. C. S.

α-Anthraquinonesulphenic Acid. Karl Fries (*Ber.*, 1912, 45, 2965—2973).—The author has succeeded in obtaining in the anthracene group, halogen thiols of the type recently described by Zincke (Abstr., 1911, i, 368; this vol., i, 762). The α- and β-chloro- and bromo-thiolanthraquinones resemble in general properties the analogues previously described, but the α-compounds are relatively more stable; also with alcohols the α-compounds react in an unusual manner with formation of alkyloxy-sulphur derivatives which behave as esters of, and are hydrolysable to, a feebly acetic substance,

$$C_6H_4<^{CO}_{CO}>C_6H_3\cdot SOH.$$

This is the first substance of this type to be isolated, and the generic name *sulphenic acid* is suggested. It is possible that the free substance is in reality a ψ-acid, and that the salts are of the structure $R\cdot S\leqslant^{X}_{O}$, where X represents the metal atom.

[With E. Engelbertz.]—When α-anthraquinone disulphide suspended in chloroform is treated with the theoretical quantity of bromine or chlorine, α-*bromothiolanthraquinone* (α-*anthraquinonesulphenyl bromide*), orange needles, m. p. 214°, or α-*chlorothiolanthraquinone* (α-*anthraquinonesulphenyl chloride*), orange needles, m. p. 224°, is respectively obtained. The substances agree in chemical behaviour; aqueous alkali slowly attacks them, forming α-anthraquinonesulphinic acid together with the original disulphide; alcoholic potassium hydroxide gives the same result more rapidly, but the products are accompanied by a little of the alkali salt of the sulphenic acid, which colours the solution bluish-green. They react in the usual manner with ammonia, amines, and phenols, for example, the bromine compound when heated with β-naphthol gives hydrogen bromide and α-*anthraquinonyl* α-[β-*hydroxynaphthyl*]-*sulphide*, golden-yellow tablets, m. p. 254°; the *alkali* salts form bronze, prismatic needles.

If the above chlorine or bromine compounds are boiled for some

time with methyl alcohol, orange-red needles of *methyl a-anthraquinonesulphenate*, m. p. 189°, separate; this substance gives a red solution in acetic acid, which turns yellow on boiling with the formation of *a*-anthraquinone disulphide and disulphoxide, together with some of the sulphinic acid. Ethyl alcohol acts on the above halogen compounds, producing *ethyl a-anthraquinonesulphenate*, red needles, m. p. 149°. If the above methyl ester is boiled for a short time with an alcoholic solution of potassium hydroxide, the *potassium* salt separates in short, almost black needles with a feeble green lustre; the aqueous solution of this salt on acidification with acetic acid deposits the free *a-anthraquinonesulphenic acid*, $C_6H_4<{}^{CO}_{CO}>C_6H_3\cdot SOH$, which crystallises from aqueous acetone in red needles, which do not melt even at 300°, although decomposition has occurred; the *alkali* salts are easily soluble in water, the *lead* and *barium* salts sparingly so, the colour of the solid in all cases being black with a feeble green lustre. The acid reacts with hydrogen chloride and bromide, forming the above anthraquinonyl sulphur chloride and bromide; with methyl sulphate in methyl-alcoholic solution it yields the methyl ester, but when shaken in alcoholic alkaline solution with methyl sulphate there is produced *methyl a-anthraquinonyl sulphoxide*, $C_6H_4<{}^{CO}_{CO}>C_6H_3\cdot \underset{\underset{O}{||}}{S}Me$, yellow needles, m. p. 226°, which by warming with hydrobromic acid gives *methyl-a-anthraquinonyl sulphide*, yellow needles, m. p. 218°; this substance is also obtainable by the action of methyl sulphate on *a*-anthraquinone mercaptan, and on oxidation with nitric acid (D 1·4) or hydrogen peroxide it regenerates the sulphoxide. Oxidation of the alcoholic alkaline solution of sulphenic acid by potassium ferricyanide gives rise to *a-anthraquinonesulphinic acid*, needles, which do melt below 300°; the same oxidation occurs slowly when an alkaline solution of the acid is exposed to air; on boiling its acetic acid solution, the sulphinic acid undergoes simultaneous oxidation and reduction to *a*-anthraquinonesulphonic acid and a mixture of the disulphide and disulphoxide respectively. The sulphenic acid when its acetic acid solution is boiled undergoes similar decomposition to its methyl ester. It is reduced by sodium sulphide to *a*-anthraquinone mercaptan, and condenses with phenols when heated, for example, giving the above *a*-anthraquinonyl *a*-[β-hydroxynaphthyl]-sulphide with β-naphthol.

D. F. T.

[Preparation of Anthracene Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 250273).—When substituted anthraquinonesulphonic acids are condensed in aqueous solution with arylmercaptols, products are formed which contain at least one sulphonic group. The *compounds* from *p*-tolyl mercaptan with 1 : 4-dichloroanthraquinone-6-sulphonic acid (a yellowish-red powder) and with 1 : 5-diamino-4 : 8-dibromoanthraquinone-2 : 6-disulphonic acid (a glistening, bronze, crystalline powder) are described together with their tinctorial properties.

F. M. G. M.

Cold Vulcanisation of Caoutchouc. GUSTAV BERNSTEIN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 185—191).—If the gelatinous substance

obtained by the action of sulphur monochloride on purified Para caoutchouc in xylene solution at room temperature is extracted in a Soxhlet apparatus with benzene, then with carbon disulphide, and finally with ethyl alcohol according to the procedure adopted by Weber, the residual product is found to contain much larger quantities of sulphur and chlorine than that which is obtained after extraction with carbon disulphide only. The latter method yields a yellow powder which contains sulphur and chlorine in approximate agreement with the formula $(C_{10}H_{16})_2S_2Cl_2$. The higher values yielded by the product obtained by extracting according to Weber's method are shown to be due to decomposition of the substance under the influence of hot benzene and alcohol

From more dilute xylene solutions, the substance resulting from the action of sulphur chloride or caoutchouc separates in the form of a powder, and under these conditions the influence of large variations in the relative quantities of the two substances has been examined. In all cases, the product appears to be that represented by $(C_{10}H_{16})_2S_2Cl_2$.

It is shown that the changes occurring in the xylene solution can be followed by measurements of the viscosity. H. M. D.

Theory of the Vulcanisation of Caoutchouc. F. Willy Hinrichsen and Erich Kindscher (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 191—193).—The product obtained by the action of sulphur on caoutchouc in cumene solution at 170° has been found to correspond with the formula $C_{10}H_{16}S_2$. The composition of the dark brown powder, which is obtained, remains practically unchanged when the ratio of caoutchouc to sulphur is varied from 2 : 1 to 1 : 4.

Certain statements made by Spence and Young (this vol., ii, 706), and by Loewen (this vol., ii, 914, 215) are subjected to criticism.

H. M. D.

The Cerebrosides of the Brain. Phœbus A. Levene and Walter A. Jacobs (*J. Biol. Chem.*, 1912, 12, 389—398).—Many cerebrosides (galactosides) have been described by various workers, and in most cases each has received several names. An attempt is made to unravel the resulting confusion. The list is finally reduced to three, but they differ only in optical activity, and in solubilities which enable their separation to be accomplished with some difficulty; it is proposed that as the real difference is stereochemical to substitute a new nomenclature, namely, *d*-cerebrin (= cerebrin, cerebron, and phrenosin of other writers), *dl*-cerebrin (= kerasin and homocerebrin of other writers), and *l*-cerebrin. W. D. H.

Thiocarbimides: the Glucoside of Cheirolin. Wilhelm Schneider and Wilhelm Lohmann (*Ber.*, 1912, 45, 2954—2961).—It has already been conjectured (Schneider, Abstr., 1910, i, 658) that cheirolin is present in wallflower seeds in the form of a glucoside. This can actually be isolated by extracting dry fat-free wallflower seed with alcohol; the glucoside, which could not be obtained pure, is a brown, hygroscopic powder, the solution of which is turned greenish-yellow by alkali. It contains the elements sulphur, nitrogen, and potassium apparently in the atomic proportions 3 : 2 : 1;

the sulphur appears to be present in three different forms, as hydrolysis with hydrochloric acid produces hydrogen sulphide (from the thiocarbimide group of cheirolin) and sulphuric acid, whilst the sulphone group (present in cheirolin) can only be detected by oxidation with fuming nitric acid. After hydrolysis with hydrochloric acid, the presence of dextrose could be detected by the formation of the osazone. The glucoside also, like sinigrin, undergoes scission when treated with silver nitrate, producing dextrose and a precipitate, *cheirolin silver sulphate*, $C_5H_9O_2NS_2,Ag_2SO_4$, which, however, is not merely a double salt. After oxidation of the glucoside with fuming nitric acid, barium methanesulphonate can be isolated. Myrosin from white mustard seed hydrolyses the glucoside, and cheirolin can be easily isolated from the product; on the other hand, wall-flower seeds, as also cauliflower seeds, contain an enzyme which is capable of liberating mustard oil from black mustard seed (myrosin free). D. F. T.

Oxidation of Picrotoxin. GEORGE BARGER and REGINALD W. L. CLARKE (*Ber.*, 1912, 45, 3166—3167. Compare Sielisch, this vol., i, 790).—On oxidation of picrotoxin by boiling with concentrated nitric acid, an *acid* is obtained sparingly soluble in warm acetic acid, and crystallising in large, tabular crystals, decomp. 300°. The acid, $C_{13}H_{14}O_9$, is dibasic. E. F. A.

Picrotin. PAUL HORRMANN and KARL SEYDEL (*Ber.*, 1912, 45, 3080—3086. Compare Sielisch, this vol., i, 790).—It has been shown previously that picrotin possesses the properties of a lactone, although neither the corresponding acid nor any of its derivatives could be isolated. The authors now find that the action of potassium hydroxide or methoxide in methyl alcohol solution gives rise to two isomeric monobasic acids, $C_{15}H_{20}O_8$, which are termed γ- and δ-picrotic acids. The latter is isolated in the form of its methyl ester, whilst the γ-acid separates out from the reaction product as the potassium salt. Exactly similar results were obtained by the action of potassium hydroxide and ethoxide in ethyl alcoholic solution.

The pronounced reducing properties of picrotin are not shared by the two acids, and it is, therefore, probable that the addition of water to the lactone linking is accompanied by some other change in the structure of the molecule.

γ-*Picrotic acid* forms stout crystals (decomp. 204—205°) and differs from the δ-acid in reducing alkaline permanganate. The *potassium* salt crystallises from methyl alcohol in slender needles containing the solvent (1 mol.), and has $[\alpha]_D^{17.5}$ $-3°57'$ in aqueous solution; it sinters and becomes brown at 245° (decomp. 260°).

δ-*Picrotic acid*, prepared by the hydrolysis of its esters with aqueous sodium hydroxide, has $[\alpha]_D^{17.5}$ $+71°58'$ (decomp. 258°); the *methyl* ester crystallises from water in slender needles, m. p. 239°, $[\alpha]_D^{17.5}$ $+77°11'$ in alcohol; the *ethyl* ester has m. p. 199°, $[\alpha]_D^{17.5}$ $+74°25'$ in alcohol.

In addition to the above mentioned products, the action of potassium hydroxide or alkyloxides on picrotin leads to the formation of a substance, $C_{15}H_{18}O_7$, *picrotin-lactone*, which is isomeric with picrotin,

and is also produced during the hydrolysis of the esters of δ-picrotic acid.

The action of excess of alkali on picrotin yields a dibasic *acid*, $C_{15}H_{22}O_9$. F. B.

Hydroxycarboxylic Esters of Coumarone, Thionaphthen, and Indole, and their Products of Alkylation. KARL VON AUWERS (*Annalen*, 1912, **393**, 338—383).—The chief interest of the paper lies in the alkylation experiments. Ethyl 2-hydroxycoumarilate (*acetate*, $C_6H_4<\genfrac{}{}{0pt}{}{C(OAc)}{O}>C\cdot CO_2Et$, m. p. 76—77°; *benzoate*, m. p. 124°) and the corresponding thionaphthen and indole derivatives yield mainly *O*-ethers by treatment with methyl sulphate or ethyl sulphate and aqueous alkali, their formation being attributed to the interaction of the ions of the alkyl sulphate and of the sodium derivative of the strongly acidic hydroxy-ester. Alkylation by an alkyl iodide and sodium alkyloxide yields mainly the *C*-ether (except in the case of ethyl 2-hydroxythionaphthen-1-carboxylate, where the *O*-ether is the main product), produced by the addition of the alkyl iodide and subsequent elimination of sodium iodide.

Whilst the parent substances are stable, their ethers are easily hydrolysed or decomposed by boiling alcoholic alkalis; the *O*-ethers yield the corresponding carboxylic acids (from which 2-alkyloxy coumarone and the corresponding thionaphthen and indole derivatives are easily obtained by heating, and coumaranone and the corresponding thionaphthen and indole derivatives by the action of acids), and the *C*-ethers experience rupture of the heterocyclic nucleus in the case of the thionaphthen compound and yield 1-alkylcoumaranones from the coumarone derivatives.

Thus by treatment at 0° with methyl sulphate and 15% potassium hydroxide, the former being always in excess, ethyl 2-hydroxycoumarilate yields almost entirely *ethyl 2-methoxycoumarilate*,

$$C_6H_4<\genfrac{}{}{0pt}{}{C(OMe)}{O}>C\cdot CO_2Et,$$

m. p. 59°, This ether yields coumaranone by treatment with boiling oxalic acid solution or 1% sulphuric acid, and *2-methoxycoumarilic acid*, $C_{10}H_8O_4$, m. p. 166—170° (decomp.), by hydrolysis with alcoholic alkalis; above its m. p. the acid yields *2-methoxycoumarone*, b. p. 109—110°/17 mm., $D_4^{19\cdot4}$ 1·1442. Ethyl 2-hydroxycoumarilate, ethyl sulphate, and aqueous potassium hydroxide at about 30° yield *2-ethoxycoumarilic acid*, m. p. 166—170° (decomp.) (*ethyl* ester, b. p. 180°/13 mm., $D_4^{14\cdot6}$ 1·1678, from the silver salt and ethyl iodide), from which coumaranone and *2-ethoxycoumarone*, b. p. 117°/16 mm., $D_4^{17\cdot2}$ 1·1068, are obtained by methods similar to those above.

Ethyl 2-hydroxycoumarilate, methyl-alcoholic sodium methoxide (1 mol.), and methyl iodide (2—3 mols.), heated in a sealed tube at 100° for one and a-half to two hours, yield almost entirely *ethyl 1-methylcoumaranone-1-carboxylate*, $C_5H_4<\genfrac{}{}{0pt}{}{CO}{O}>CMe\cdot CO_2Et$; this, however, could not be isolated as such, but was converted by aqueous alcoholic sodium hydroxide into 1-methylcoumaranone, identified by its disemicarbazide

derivative, m. p. 234—235°. An unsuccessful attempt was made to prepare the pure *C*-methyl ether by heating salicylaldehyde, methyl α-bromopropionate, and alcoholic sodium ethoxide on the water-bath, hydrolysing the resulting *ethyl* α-o-*aldehydophenoxypropionate*,

$$CHO{\cdot}C_6H_4{\cdot}O{\cdot}CHMe{\cdot}CO_2Et,$$

b. p. 181—183°/19 mm. (*semicarbazone*, m. p. 120°, after drying at 100°), oxidising the *acid*, m. p. 63—73°, by potassium permanganate to α-salicyloxypropionic [α-*o*-carboxyphenyloxypropionic] acid, m. p. 136°, and treating the *ethyl* ester, b. p. 192—194°/17—18 mm., of this in benzene with sodium. By treatment with ethyl iodide and alcoholic sodium ethoxide, ethyl 2-hydroxycoumarilate yields *ethyl* 1-*ethyl coumaranone*-1-*carboxylate* (containing a little of the *O*-ether), b. p. 173·5—178·5°/17 mm., $D_4^{19\cdot8}$ 1·1537, when prepared at atmospheric pressure, b. p. 170—175°/15 mm., D_4^{18} 1·1563, when prepared in a sealed tube, which is converted into 1-ethylcoumaranone by treatment with alcoholic alkali.

The following substances are the intermediate compounds required in the preparation of *ethyl 2-hydroxy-4-methylcoumarilate*,

$$C_6H_3Me{<}\begin{matrix}C(OH)\\O\end{matrix}{>}C{\cdot}CO_2Et,$$

m. p. 96°, long, white needles (*acetate*, m. p. 68—68·5°; *benzoate*, m. p. 126°): *ethyl 2-aldehydo*-p-*tolyloxyacetate*,

$$CHO{\cdot}C_6H_3Me{\cdot}O{\cdot}CH_2{\cdot}CO_2Et,$$

m. p. 54·5°, prepared from *p*-homosalicylaldehyde and ethyl bromoacetate, and the corresponding *acid*, $C_{10}H_{10}O_4$, m. p. 151°, white needles; p-*homosalicyloxyacetic* [o-*carboxy*-m′-*tolyloxyacetic*] *acid*, $CO_2H{\cdot}C_6H_3Me{\cdot}O{\cdot}CH_2{\cdot}CO_2H$, m. p. 182—183°, and its *diethyl* ester, b. p. 195°/15 mm., the coumarone derivative being obtained by the action of sodium on the latter in dry benzene. By treatment with methyl sulphate and 10% potassium hydroxide at the ordinary temperature, ethyl 2-hydroxy-4-methylcoumarilate yields *ethyl 2-methoxy-4-methylcoumarilate*, $C_6H_3Me{<}\begin{matrix}C(OMe)\\O\end{matrix}{>}C{\cdot}CO_2Et$, b. p. 199°/18 mm., m. p. 29—30° (after long keeping), $D_4^{22\cdot7}$ 1·1702; the *acid*, $C_{11}H_{10}O_4$, m. p. 178—180°, is obtained by hydrolysing the preceding ester by alcoholic alkali or by treating ethyl 2-hydroxy-4-methylcoumarilate with an excess of alkali and methyl sulphate. The acid yields *2-methoxy-4-methylcoumarone*, b. p. 149°/36 mm., $D_4^{24\cdot3}$ 1·1074, above its m. p. *2-Ethoxy-4-methylcoumarilate*, $C_{12}H_{12}O_4$, m. p. 173°, prepared by gently warming ethyl 2-hydroxy-4-methylcoumarilate with ethyl sulphate and aqueous alkali, forms an *ethyl* ester, m. p. 47—48° (from the silver salt), and yields *2-ethoxy-4-methylcoumarone*, b. p. 133°/15·5 mm., $D_4^{16\cdot5}$ 1·0827, by loss of carbon dioxide.

1 : 4-*Dimethylcoumaranone*, $C_6H_3Me{<}\begin{matrix}CO\\O\end{matrix}{>}CHMe$, m. p. 63° (disemicarbazide derivative, m. p. 225°), and *ethyl* 1 : 4-*dimethylcoumaranone*-1-*carboxylate*, $C_6H_3Me{<}\begin{matrix}CO\\O\end{matrix}{>}CMe{\cdot}CO_2Et$, are obtained by heating ethyl 2-hydroxy-4-methylcoumarilate with methyl iodide and methyl-alcoholic sodium methoxide. The ester has b. p. 170—172°/15 mm., $D_4^{20\cdot1}$ 1·1606, when prepared at atmospheric pressure, and

b. p. 179—182°/18·5 mm., $D_4^{24·1}$ 1·1533, when obtained in a sealed tube; it contains a little of the *O*-ether, and therefore yields 2-methoxy-4-methylcoumarilic acid as well as 1 : 4-dimethylcoumaranone by warming with alcoholic alkali. In an attempt to prepare the pure ester, the following have been obtained: *a-2-aldehydo-4-methylphenoxypropionic acid*, m. p. 111—112°, and its *methyl* ester, m. p. 57°; *ethyl* ester, b. p. 206°/35 mm., and *oxime*, m. p. 168—169°, from the last *a-2-cyano-4-methylphenoxypropionic acid*, m. p. 121—122°, being obtained by boiling acetic anhydride.

The ethylation of ethyl 2-hydroxy-4-methylcoumarilate by ethyl iodide and alcoholic sodium ethoxide in a sealed tube yields a mixture of the *O*- and the *C*-ethers, since the product yields with boiling alcoholic alkali 4-*methyl*-1-*ethylcoumaranone*, m. p. 40°, and 2-ethoxy-4-methylcoumarilic acid.

Methyl 2-hydroxythionaphthen-1-carboxylate, methyl-alcoholic sodium methoxide (1 mol.), and methyl iodide (2 mols.), heated in a sealed tube at 100° for two hours, yield a mixture of *methyl 2-methoxythionaphthen-1-carboxylate*, $C_6H_4<\underset{S}{\overset{C(OMe)}{}}>C·CO_2Me$, m. p. 68—68·5°; and *methyl 2-keto-1-methyldihydrothionaphthen-1-carboxylate*,

$$C_6H_4<\underset{S}{\overset{CO}{}}>CMe·CO_2Me,$$

m. p. 74°, which is separated by the sparing solubility of the latter in petroleum of low b. p., or in methyl alcohol. The *O*-ether, which is the chief product by this method of methylation, is the only product when an aqueous alkali and an excess of methyl sulphate are used; it yields 2-*methoxythionaphthen*-1-*carboxylic acid*, m. p. 171—173°, by hydrolysis by alcoholic alkali. This acid is readily converted into 2-methoxythionaphthen above its m. p. The *C*-ether is rapidly decomposed by cold alcoholic alkali, yielding *a-o-carboxyphenylthiolpropionic acid*, $CO_2H·C_6H_4·S·CHMe·CO_2H$, m. p. 194—195°, colourless leaflets, which is also obtained from thiosalicylic acid and a-bromopropionic acid and dilute sodium hydroxide on the water-bath; it cannot be transformed back to the thionaphthen derivative.

Methyl 2-hydroxythionaphthen-1-carboxylate reacts with ethyl iodide and sodium ethoxide at 100° in a sealed tube to form a mixture of the *O*- and the *C*-ethyl ethers. Since these could not be separated, the product was treated with alcoholic alkali, whereby the former yields 2-*ethoxythionaphthen*-1-*carboxylic acid*, m. p. 158°, stout prisms, and the latter is converted into *a-o-carboxyphenylthiolbutyric acid*,

$$CO_2H·C_6H_4·S·CHEt·CO_2H,$$

m. p. 171—172°. 2-*Ethoxythionaphthen* has b. p. 154°/19 mm., and $D_4^{17·6}$ 1·1591.

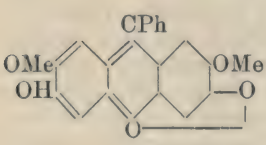
Ethyl indoxylate, methyl sulphate, and dilute potassium hydroxide at the ordinary temperature yield *ethyl 3-methoxyindole-2-carboxylate*, $C_6H_4<\underset{NH}{\overset{C(OMe)}{}}>C·CO_2Et$, m. p. 92—93°; by hydrolysis with alcoholic alkali, the ester yields the *acid*, $C_{10}H_9O_3N$, m. p. 147—148° (decomp.), which is converted by heating into 3-*methoxyindole*, m. p. 69—70°, b. p. about 170°/18—19 mm., flattened needles. Methoxyindole develops a brownish-violet coloration with concentrated sulphuric

acid, produces a brownish-red coloration on a pine shaving moistened with hydrochloric acid, and yields indigotin by warming with ferric chloride and hydrochloric acid.

The methylation of ethyl indoxylate by methyl iodide and methyl alcoholic sodium methoxide at 100° in a sealed tube yields a mixture of methylated derivatives which has not yet been thoroughly examined. C. S.

Ethers of Hydroxyquinolbenzein [2 : 3 : 7-Trihydroxy-9-phenylfluorone]. FRIEDRICH KEHRMANN and M. GÜNTHER (*Ber.*, 1912, **45**, 2884—2891).—An examination of the oxonium haloids obtained from substituted phenylxanthhydrols would indicate that the presence of an esterified carboxyl group in the ortho-position in the phenyl group is essential for the existence of normal haloid salts (compare Kehrmann and Dengler, Abstr., 1909, i, 249; Gomberg and Cone, *ibid.*, 1910, i, 55; Kehrmann and Knop, this vol., i, 43). That this is not so is proved by the following example.

2 : 3 : 7-Trihydroxy-9-phenylfluorone is readily obtained in 70% yield by keeping equal weights of hydroxyquinol and benzotrichloride for twenty-four hours at the ordinary temperature, for eighteen hours at 60—70°, and finally for one hour at 100°, and decomposing the resulting chloride by boiling water. When heated with the calculated amount of dilute aqueous sodium hydroxide and an excess of methyl iodide, the benzein yields a mixture of 3-*hydroxy*-2 : 7-*dimethoxy*-9-*phenylfluorone* (annexed formula), m. p. 287—288°, dark red crystals with blue metallic reflex, and the corresponding *trimethyl ether*, $C_{22}H_{18}O_5$, m. p. 277°, golden leaflets. The dimethyl ether forms a red *sodium* salt, and a *chloride*, orange-red leaflets, and *acetate*, both of which are hydrolysed by water; the *acetate* of the trimethyl ether does not give a precipitate by the addition of water to its solution in acetic acid.

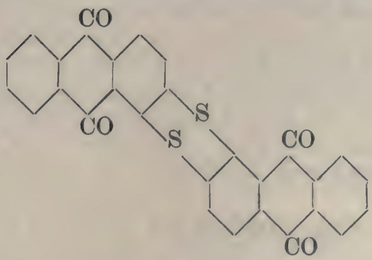


By treating the trimethyl ether in nitrobenzene at 150° with methyl sulphate, a tetramethyl ether is obtained, which is isolated by hydrochloric acid in the form of 2 : 3 : 6 : 7-*tetramethoxy*-9-*phenylxanthonium chloride*, $C_6H_2(OMe)_2{<}^{CPh}_{OCl}{>}C_6H_2(OMe)_2$, red leaflets. The corresponding *platinichloride*, $2C_{23}H_{21}O_5,PtCl_6$, brick-red leaflets, and *dichromate* are described. The chloride dissolves in water without hydrolysing. The solution is bitter, and remains unchanged for a short time even after the addition of sodium hydrogen carbonate, but ultimately decomposes, yielding the *tetramethoxyphenylxanthenol*, colourless needles (*methyl alcoholate*, m. p. 171—172°). An ethereal solution of the carbinol forms with carbon dioxide a yellow, fluorescent solution, which probably contains the *xanthonium carbonate*. C. S.

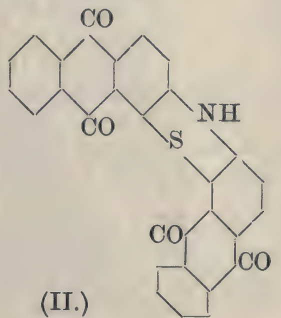
Action of Hydrogen Peroxide on Trithienyl. MAURICE LANFRY (*Compt. rend.*, 1912, **155**, 836—838).—By the action of hydrogen peroxide (10 vols.) on a boiling solution of trithienyl in

dilute acetic acid two compounds are formed according to the duration of the reaction. After thirty minutes, a *compound*, $C_{12}H_8S_2O_2$, m. p. 231—233°, is obtained, crystallising in colourless prisms, insoluble in water, but soluble in benzene or chloroform. It is not acted on by aqueous alkalis or dilute sulphuric acid. If the reaction is prolonged to one hour, the compound, $C_{12}H_8S_2O_4$, m. p. 338°, already prepared by Renard (compare Abstr., 1891, 427) by the oxidation of trithienyl with fuming nitric acid, is obtained. It is not acted on by bromine in the cold or on heating. W. G.

Preparation of Anthraquinone Derivatives Containing Sulphur. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248171).—When 1 : 2-dihalogen- or 1 : 2-halogenamino-anthraquinones are boiled during some hours in nitrobenzene solution with 1 : 2-dimercaptol- or 1 : 2-aminomercaptol-anthraquinones condensation occurs.



(I.)



(II.)

Diphthalylthianthren (formula I.), red needles with a metallic lustre, is thus prepared from anthraquinone-1 : 2-dimercaptol and 1 : 2-dichloroanthraquinone, whilst 1 : 2-dichloroanthraquinone and 2-aminoanthraquinone-1-mercaptol furnishes *thiodianthraquinonylamine* (formula II.).

A complete analysis of these compounds is given in the original.

F. M. G. M.

Preparation of Compounds from Quinine and Dialkylbarbituric Acids. EMANUEL MERCK (D.R.-P. 249908).—A salt from codeine and diethylbarbituric acid has previously been prepared (compare this vol., i, 209), and the reaction has now been extended to other nearly related alkaloids.

Quinine diethylbarbiturate crystallises in fine needles, m. p. 136°, whilst *quinine dipropylbarbiturate* forms colourless needles, m. p. 127—128°. F. M. G. M.

Preparation of Esters of Hydroquinine. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 250379. Compare Abstr., 1888, 69, and 1911, ii, 219).—*Hydroquinine ethyl carbonate*, tasteless, colourless needles, m. p. 75—78°, is prepared by boiling together equimolecular proportions of hydroquinine and ethyl chlorocarbonate in benzene solution during ten minutes.

Benzoylhydroquinine, colourless crystals, m. p. 102—107°, is obtained

by the reaction of benzoyl chloide on hydroquinone; it forms a *salicylate*, colourless needles, m. p. 193·5°.

Hydroquinine salicylate, large, colourless crystals, m. p. 115—119°, is prepared by heating hydroquinine with salol during six hours at 130—140°.

p-*Nitrobenzoylhydroquinine*, m. p. 163—164°, is obtained by the action of *p*-nitrobenzoyl chloride on hydroquinine in boiling benzene solution; on reduction it furnishes *p-aminobenzoylhydroquinine*, yellow needles, m. p. 155—157·5°. *Hydroquinine carbonate* is prepared by the action of carbonyl chloride on hydroquinine; these compounds are of therapeutic value. F. M. G. M.

Peculiar Relation between the Strengths of Acids and their Activity. II. Paul Rabe [with Eberhard Felle] (*Ber.*, 1912, **45**, 2927—2932. Compare Rabe and McMillan, Abstr., 1911, ii, 33).—The author has extended his previous work on the catalytic influence of acids in accelerating the conversion of cinchonine into cinchotoxine, and has now examined the effect of hydrochloric and acetic acids on cinchonine, cinchonidine, hydrocinchonine, quinine, quinidine, and hydroquinine. Hydrochloric acid did not effect the transformation in any of the observed cases. The change, however, takes place slowly in dilute alcoholic solution (80%), and still more slowly in benzene solution.

In the case of narcotine, the following reactions are possible: (1) racemisation with the formation of so-called gnoscopine; (2) hydrolysis to nornarceine; (3) hydrolytic decomposition into cotarnine and meconine (compare Rabe and McMillan, Abstr., 1911, i, 77). On treatment with 3*N*-acetic acid at 98° during thirty hours, narcotine yields small quantities of nornarceine, meconine, and cotarnine, together with traces of gnoscopine; with *N*-hydrochloric acid, on the other hand, no decomposition product was obtained after treatment during ten hours at 98°, whilst, after thirty hours, only traces of nornarceine were detected.

Choline when heated at about 98° during seventy-two hours with *N*-hydrochloric and *N*-acetic acids respectively yielded 70% and 66% of unchanged material. Trimethylamine could not be detected. A portion of the choline apparently suffered change in some unknown direction.

Oleic acid when heated with acetic acid or with acetic acid and water at 98° during thirty-six hours was not converted into elaidic acid. H. W.

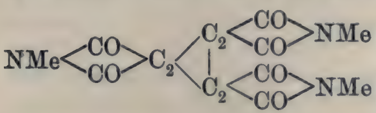
Hæmanthine. Louis Lewin (*Arch. expt. Path. Pharm.*, 1912, **70**, 302).—Polemical against Tutin (this vol., i, 797). Hæmanthine (from *Haemanthus toxicarius* [*Buphane disticha*]) is a pure substance with characteristic chemical reactions, and a constant toxic action.

W. D. H.

Preparation of *apo*Scopolamine. F. Hoffmann, La Roche & Co. (D.R.-P. 247819).—apo*Scopolamine*, $C_{17}H_{19}O_3N$, needles, m. p. 97—98°, is readily prepared by dissolving two parts of scopolamine

sulphuric acid (this vol., i, 896) in hot water (50 parts), cooling until crystallisation commences, and then adding 20 parts of 2*N*-sodium hydroxide, when the product separates after half an hour in crystalline form; it furnishes a crystalline *nitrate*. *Chloroscopolamine* is obtained by the action of thionyl chloride on scopolamine. F. M. G. M.

Derivatives of Triketopyrrolidine and their Conversion into Trimethylparamide. Otto Mumm and Clemens Bergell (*Ber.*, 1912, 45, 3149—3155).—By the action of potassium oxalate on the additive product of methyl sulphate and *a*-methyl*iso*oxazole an *N*-oxalyl compound, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot NMe\cdot CO\cdot CO_2K$, is obtained, which immediately loses water, forming *triketo*-3-*acetyl*-1-*methylpyrrolidine*, $CH_3\cdot CO\cdot CH<\begin{matrix}CO\cdot NMe\\ | \\ CO\cdot CO\end{matrix}$. The *potassium* salt at first formed is readily hydrolysed by acids. The corresponding *benzoyl* derivative is prepared in a similar manner from 2-phenyl*iso*oxazole. Both acyl compounds have acid properties; they are colourless, but form yellow salts. With phenylhydrazine, the benzoyl derivative forms an additive compound, which is converted into the phenylhydrazone when boiled with alcoholic hydrogen chloride.



The benzoyl compound is not affected by boiling with water, but the acetyl derivative loses acetic acid, forming a polymeride of the methylimide of acetylenedicarboxylic acid, namely, *trimethylparamide*, which may be regarded as the trimethylimide of mellitic acid (annexed formula).

It is assumed that in the acyl compounds the oxalic acid residue is attached to nitrogen. Proof of this is afforded by the formation of 3-*methyl*-2-*acetonyl*-4-*quinazolone*, $C_6H_4<\begin{matrix}CO\cdot NMe\\ | \\ N{=}C\cdot CH_2\cdot CO\cdot CH_3\end{matrix}$, when sodium anthranilate acts on the methyl sulphate additive product of *a*-methyl*iso*oxazole. When boiled with dilute hydrochloric acid, acetic acid is eliminated and 2 : 3-dimethylquinazolone, $C_6H_4<\begin{matrix}CO\cdot NMe\\ | \\ N{=}CMe\end{matrix}$, is obtained.

The *potassium* salt of *triketo*-3-*benzoyl*-1-*methylpyrrolidine* crystallises in yellow, interlaced needles, m. p. 175°, and yields when acidified the *triketopyrrolidine* itself, m. p. 107°. The *additive product* with phenylhydrazine has m. p. 143°; the *phenylhydrazone* forms yellow prisms, m. p. 165°.

Triketo-3-*acetyl*-1-*methylpyrrolidine* separates in almost colourless prisms, m. p. 120—124°; the *potassium* salt is yellow.

Trimethylparamide crystallises in slender, colourless needles, subliming at about 400°.

3-*Methyl*-2-*acetonyl*-4-*quinazolone* crystallises in colourless rods, m. p. 198°. E. F. A.

The Blood Pigment. X. J. Grabowski and Leon Marchlewski (*Zeitsch. physiol. Chem.*, 1912, 81, 86—89).—It is probable that methyl ethylpyrrole is a constituent of hæmopyrrole.

3-Methyl-4-*n*-propylpyrrole, prepared from methyl-*n*-propylmaleic anhydride, distils in oily drops. In aqueous solution it gives a red coloration with Ehrlich's reagent, and a white precipitate with mercuric chloride. In ethereal solution it reacts with diazonium chloride; the product consists of dark blue crystals with a coppery lustre, m. p. 253°, and slender needles, m. p. 225°. The corresponding compounds from 3-methyl-4-ethylpyrrole have m. p. 264° and 233°, whereas similar compounds from hæmopyrrole show m. p. 268° and 233°. E. F. A.

Action of Sodium Alkyloxides on Esters of Pyrrole-carboxylic Acids. II. and III. U. Colacicchi and C. Bertoni (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 450—454, 518—523. Compare this vol., i, 647).—II. When sodium ethoxide (10%) and ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate are heated for fourteen to sixteen hours at 220°, it is possible to separate from the reaction product by extraction with ether and fractional distillation, a dimethyldiethyl-pyrrole, which yields a picrate, m. p. 88—89°, identical with that of Fischer and Bartholomäus (this vol., i, 384). The *dimethyldiethyl-pyrrole* obtained from this picrate is an almost colourless oil, b. p. 112—114°/22 mm. It has an odour resembling that of thymol; it does not give the pine-splinter or Ehrlich reactions. The picrate prepared from it has m. p. 92°.

The action of sodium ethoxide on 3-acetyl-2 : 4-dimethylpyrrole (twelve hours at 150—170°) also yields among other substances the tetra-substitution product, which was isolated as picrate.

III. When ethyl 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate is heated with sodium ethoxide (10%) for fourteen hours at 220—230°, a *dimethyldiethylpyrrole* is formed. Its *picrate*, $C_{16}H_{20}O_7N_4$, crystallises in yellow prisms, m. p. 102—103°.

When an ethereal solution of benzoyl chloride is added to the product of the reaction between magnesium methyl iodide and 2 : 3 : 5-trimethylpyrrole, 3-*benzoyl*-2 : 4 : 5-*trimethylpyrrole*, $C_{14}H_{15}ON$, is obtained. It crystallises in somewhat red needles, m. p. 172—173°, and is identical with the substance prepared from oximinomethyl ethyl ketone and benzoylacetone by Knorr's method. R. V. S.

Some Acyl Derivatives of 2- and 3-Aminopyridines. F. Carlo Palazzo and G. Marogna (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 512—518. Compare Palazzo and Tamburini, Abstr., 1911, i, 327). —When 3-aminopyridine is treated with ethyl acetoacetate under the same conditions as were employed by Palazzo and Tamburini, 3-*aceto-acetylaminopyridine* is obtained, m. p. 134—135° (previously softening). It is soluble in acids and alkalis, gives a green precipitate with ammoniacal copper acetate, and an intense reddish-violet coloration with ferric chloride. 3-*Benzoylacetylaminopyridine* has m. p. 100—101° (softening at 96°), and has properties similar to those of the aceto-derivative.

2-Aminopyridine reacts with ω-bromoacetophenone (preferably in alcoholic solution), forming the *compound*, $C_5H_4N \cdot NH \cdot CH_2 \cdot COPh$, which crystallises in silky needles, m. p. 135°. R. V. S.

Preparation of the Hydrochlorides of Quinoline- and Pyridine-Iodochlorides. MORITZ KOHN and ARTUR KLEIN (*Monatsh.*, 1912, 33, 967—970).—When a mixture of quinoline with diluted nitric acid and iodine is heated to boiling and concentrated hydrochloric acid added gradually, the brown colour of the iodine disappears, and an oil separates which crystallises on cooling; this substance is the hydrochloride of quinoline, iodochloride, C_9H_7N,ICl,HCl, m. p. 118—120° (compare Dittmar, Abstr., 1886, 158; Pictet and Krafft, Abstr., 1892, 1356); the substance is readily hydrolysed by water with the formation of the free quinoline iodochloride, m. p. 156—157°.

In a similar manner, pyridine yields the hydrochloride of pyridine iodochloride, m. p. 183°. D. F. T.

Preparation of Condensation Products of Cyclic Ammonium Bases. A. KAUFMANN (D.R.-P. 250154).—Compounds of therapeutic value are obtained by the action of an alkali hydroxide or ethoxide on quaternary salts of quinoline in the presence of ethyl acetoacetate, phenylacetonitrile, or indoxyl. The *compound*, $C_{18}H_{16}N_2$, m. p. 122—125°, and having the constitution:

$$NHMe\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}CPh\cdot CN \quad \text{or} \quad C_6H_4{<}\begin{matrix}CH{=}CH \\ | \\ NMe\cdot CH\cdot CHPh\cdot CN\end{matrix}$$

is prepared from phenylacetonitrile, quinoline, methyl sulphate, and sodium ethoxide.

The *compound*, $C_{10}H_6N\cdot CH_2\cdot NO_2$, brownish-yellow needles, is obtained from quinoline, methyl sulphate, and nitromethane, whilst quinoline methiodide and ethyl acetoacetate furnish the *compound*, $C_{26}H_{28}O_3N_2$, leaf-like aggregates, m. p. 146—147°, and nitromethane with *iso*quinoline methiodide, a *product* with m. p. 99°. F. M. G. M.

4-Quinolyl Ketones. ADOLF KAUFMANN, HEINRICH PEYER, and MAX KUNKLER (*Ber.*, 1912, 45, 3090—3098).—The authors suggest that the specific action of quinine in cases of malaria is connected with the presence of the $-CH(OH)\cdot\dot{C}H\cdot N{:}$ group in the 4-position of the quinoline nucleus, and in support of this view mention that adrenaline contains the same grouping, and that the physiological properties of quinine are essentially modified by the disappearance of the hydroxyl group from the molecule.

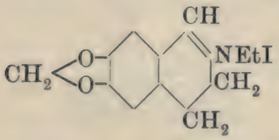
The synthesis of quinoline derivatives containing the above group in the 4-position is being undertaken; in the present paper a number of 4-quinolyl ketones are described. These form well crystallised salts, and resemble in their chemical behaviour and constitution the cinchotoxins of Miller and Rohde (Abstr., 1893, i, 434).

4-*Quinolyl methyl ketone*, $C_9H_6N\cdot COMe$, prepared by the interaction of 4-cyanoquinoline and magnesium methyl iodide, and purified by means of its *picrate*, which forms soft, yellow needles, m. p. 165—170° (decomp.), or its *acetate* (long, white needles, m. p. 70°), is a pale yellow oil, b. p. 138°/2 mm., m. p. below −20°; the *hydrochloride* forms colourless prisms, m. p. 200—214° (decomp.); the *methiodide*, dark red crystals, m. p. 172° (decomp.); the yellow *phenylhydrazone* forms a *picrate*, which crystallises from acetic acid in cinnabar-red granules, m. p. 224° (decomp.).

4-Quinolyl phenyl ketone, prepared from 4-cyanoquinoline and magnesium phenyl bromide, distils at 155°/0·5 mm., as a viscid, pale yellow oil, which solidifies to an opal-like mass, m. p. 58—59°; it crystallises from water in long, white needles, and yields a *picrate*, crystallising in brownish-yellow leaflets, m. p. 214° (decomp.), and a *phenylhydrazone*, which forms a yellow, crystalline powder, m. p. 239—240°. It is not identical with the compound, m. p. 294°, described under the same name by Remfry and Decker (Abstr., 1908, i, 364), and obtained by the action of magnesium phenyl bromide on ethyl cinchonate.

6-*Methoxy*-4-*quinolyl methyl ketone*, $OMe{\cdot}C_9H_5N{\cdot}COMe$, obtained from quinonitrile (4-cyano-6-methoxyquinoline), crystallises in thin, golden-yellow platelets, m. p. 92°, and give solutions having a yellowish-green fluorescence. F. B.

Preparation of Dihydro*iso*quinoline Derivatives. HERMAN DECKER (D.R.-P. 249723. Compare this vol., i, 581).—It is found that the physiological action of 6:7-methylenedioxy-3:4-dihydro*iso*quinoline (Abstr., 1911, i, 906) is increased by alkylation; the *ethiodide* (annexed formula) forms yellow leaflets, m. p. 220°, and the corresponding *benzyl chloride* is a pale yellow, hygroscopic, crystalline powder, m. p. 215°.



F. M. G. M.

Preparation of Compounds from 2-Phenylquinoline-4-carboxylic Acid or its Homologues with Glycine. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 249766).—When 2-phenylquinoline-4-carboxylic acid or its homologues react with the alkyl esters of glycine the corresponding salts are formed: *Ethylglycyl 2-phenylquinoline-4-carboxylate* forms pale yellow needles, m. p. 135°, whilst the corresponding *ester* of 2-phenyl-6-methylquinoline-4-carboxylic acid is a colourless, crystalline powder, m. p. 126—127°.

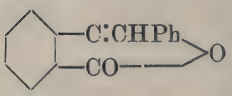
F. M. G. M.

Preparation of Substituted 2:3-Diphenylquinoline-4-carboxylic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249765).—When isatin derivatives are condensed with deoxybenzoins they yield 2:3-diphenylquinoline-4-carboxylic acids, which are colourless, crystalline, tasteless, and of therapeutic value.

2:3-*Diphenyl*-6:8-*dimethylquinoline*-4-*carboxylic acid*, colourless needles, m. p. 245°, is obtained when dimethylisatin (60 parts) in boiling 30% potassium hydroxide solution (5 parts KOH) is slowly treated with an alcoholic solution of deoxybenzoin (80 parts).

2:3-*Diphenyl*-6-*methylquinoline*-4-*carboxylic acid*, m. p. 319°, is prepared in a similar manner from deoxybenzoin with *p*-methylisatin; 3-*phenyl*-2-p-*tolylquinoline*-4-*carboxylic acid*, m. p. 304°, from isatin with *p*-methyldeoxybenzoin, whilst isatin with *p*-methoxydeoxybenzoin furnishes 3-*phenyl*-2-p-*anisylquinoline*-4-*carboxylic acid*, colourless leaflets, m. p. 291°.

3-*Phenyl*-2-o-*carboxyphenylquinoline*-4-*carboxylic acid*, colourless leaflets, m. p. 78°, is obtained by the condensation of isatin with the anhydride of deoxybenzoincarboxylic acid (annexed formula), whilst 2:4-dibromoisatin with deoxybenzoin furnishes 6:8-*dibromo*-2:3-*diphenylquinoline*-4-*carboxylic acid*, colourless needles, m. p. 250°, and 3-*phenyl*-2-p-*tolyl*-6-*methylquinoline*-4-*carboxylic acid*, colourless needles, m. p. 290°, is obtained from *p*-methylisatin with *p*-methyldeoxybenzoin. F. M. G. M.



New Derivatives of Phenyl*iso*oxazolone. André Meyer (*Compt. rend.*, 1912, 155, 841—844).—With a view to a study of the relations between colour and constitution, the author has prepared a number of derivatives of phenyl*iso*oxazolone by condensation with cyclic aldehydes according to a method previously described (compare Wahl and Meyer, Abstr., 1908, i, 368). The following condensation products (substituted 3-phenyl-4-benzylidene*iso*oxazolones) were prepared.

3-*Phenyl*-4-p-*tolylidene*iso*oxazolone*, $C_3O_2NPh:CH\cdot C_6H_4Me$, yellow needles, m. p. 177—178°, giving a deep yellow solution in sulphuric acid.

3-*Phenyl*-4-p-iso*propylbenzylidene*iso*oxazolone*,

$$C_3O_2NPh:CH\cdot C_6H_4Pr^\beta,$$

golden-yellow scales, m. p. 147—148°.

3-*Phenyl*-o-*nitrobenzylidene*iso*oxazolone*, $C_3O_2NPh:CH\cdot C_6H_4\cdot NO_2$, yellow needles, m. p. 132—133°. The meta-*isomeride* forms deep yellow crystals, m. p. 138—139°, and the para-*isomeride*, tufts of yellow needles, m. p. 179—180°.

3-*Phenyl*-4-o-*anisylidene*iso*oxazolone*, $C_3O_2NPh:CH\cdot C_6H_4\cdot OMe$, deep yellow prisms, m. p. 165—166°.

3-*Phenyl*-4-*vanillylidene*iso*ozazolone*, $C_3O_2NPh:CH\cdot C_6H_3(OH)\cdot OMe$, long, pale yellow needles, m. p. 180—181°.

3-*Phenyl*-4-op-*dihydroxybenzylidene*iso*oxazolone*,

$$C_3O_2NPh:CH\cdot C_6H_3(OH)_2,$$

deep yellow needles, m. p. 280°, only very slightly soluble in the usual solvents, giving an orange-yellow solution in alkalis.

3-*Phenyl*-4-mp-*dihydroxybenzylidene*iso*oxazolone*, brown leaflets, m. p. 202—203°, giving a reddish-violet solution in alkalis.

iso*Phthalylidene*-bis-3-*phenyl*iso*oxazolone*, $C_6H_4(CH:C_3O_2NPh)_2$, bright yellow needles, m. p. 212—213°.

3-Phenyl-4-salicylidene*iso*oxazolone gives an *acetyl* derivative, small, yellow crystals, m. p. 142—143°.

The colour of the compounds containing a free hydroxyl group is deeper than their ethers. Acetylation diminishes the depth of colour more than methylation. The position of the hydroxyl group has an influence on the colour, ortho-derivatives being generally less coloured than para-derivatives, the former, however, yielding more deeply coloured solutions in alkalis or sulphuric acid than the latter. Of the nitro-derivatives the meta possesses most colour and the ortho least. The colour is attributed to the complex $CO\cdot C:C\cdot$, the group CO being part of a pentatomic heterocyclic ring.

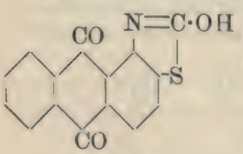
The author proposes the name "*iso*oxazole-indogenides" for these derivatives, and points out their resemblance to the corresponding pyrazole derivatives, the colour of the latter being less pronounced than that of the former. W. G.

Preparation of Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 250090).—The condensation of acyl derivatives of *o*-diaminoanthraquinones has previously been described (this vol., i, 140); it is now found that if *o*-aminoanthraquinone mercaptans are employed, the following reaction takes place, yielding anthraquinonethiazoles,

$$A{<}^{NH\cdot CO\cdot R}_{SH} \quad \text{or} \quad A{<}^{NH_2}_{S\cdot CO\cdot R} \longrightarrow A{<}^{N}_{S}{>}C\cdot R$$

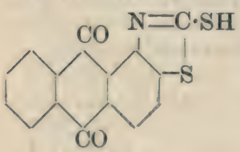
(A = anthraquinone).

The *thiazole*, obtained when sodium 1-aminoanthraquinone-2-mercaptan (1 part) is boiled with acetic anhydride (5 parts), separates in pale yellow needles.


(I.)

The *hydroxythiazole* (formula I.), small needles, m. p. 255°, is prepared from sodium-1-aminoanthraquinone-2-mercaptan with ethyl chlorocarbonate in alcoholic solution.

The *thiazolmercaptole* (formula II.), orange-yellow needles, is prepared in a similar manner in the presence of carbon disulphide, whilst 1 : 4-diaminoanthraquinone-2-mercaptol when boiled with benzoyl chloride in nitrobenzene solution furnishes 4-*benzoylaminoanthraquinone*-1 : 2-*thiazole*, brown prisms. F. M. G. M.


(II.)

Cause of the Blue Colour Produced by Nitrous Acid and Other Oxidising Agents in Sulphuric Acid Solutions of Diphenylamine. FRIEDRICH KEHRMAN and ST. MICEWICZ (*Ber.*, 1912, **45**, 2641—2653).—By boiling tetraphenylhydrazine in toluene solution, Wieland (Abstr., 1911, i, 569) obtained a yellow substance, which dissolved in sulphuric acid in the presence of oxidising agents with a blue coloration, and was considered by him to be a diphenyldihydrophenazine. The blue coloration produced in the diphenylamine reaction was referred by Wieland to the intermediate formation of this substance. The authors point out, however, that the properties of the substance differ very considerably from those of the homologous di-*p*-tolyldihydrotolazine, and thus render it improbable that the compound has the structure assigned to it by Wieland. Further, the explanations given by Wieland of the transformation of tetra-arylhydrazines into phenazonium derivatives are not in accord with the results obtained by Jacobson, who has shown that, under the influence of acids, symmetrical diarylamines containing substituents in the para-position undergo the semidine transformation, whilst unsubstituted diarylhydrazines are converted into benzidine derivatives. The

action of sulphuric acid on tetra-*p*-tolylhydrazine would thus lead to the formation of a semidine (I), which is then converted by oxidation into the *o*-indamine (II), and finally by loss of hydrogen chloride into di-*p*-tolyldihydrotolazine (III):

$$C_6H_4Me\diagup\!\!\begin{array}{l}N(C_6H_4Me)- \\ NH(C_6H_4Me)\end{array}\!\!>C_6H_3Me \qquad C_6H_4Me\diagup\!\!\begin{array}{l}N(C_6H_4Me)Cl \\ N(C_6H_4Me)\end{array}\!\!\geqslant C_6H_3Me$$

(I). (II).

$$C_6H_3Me\!<\!\begin{array}{l}N(C_6H_4Me) \\ N(C_6H_4Me)\end{array}\!\!>C_6H_3Me$$

(III).

Tetraphenylhydrazine, on the other hand, undergoes the benzidine transformation, yielding *NN'*-diphenylbenzidine, which cannot be further converted into diphenyldihydrophenazine. In order to determine the cause of the blue coloration in the diphenylamine reaction, the authors have examined the action of nitrous acid and other oxidising agents on diphenylamine and *NN'*-diphenylbenzidine, and come to the conclusion that the blue coloration is due to the formation of quinoneimonium salts of the composition

$$NPh{:}C_6H_4{\cdot}C_6H_4{:}NPh,HX,$$

produced by the oxidation of *NN'*-diphenylbenzidine, the latter compound being formed by the action of sulphuric acid on diphenylamine (compare Kadiera, Abstr., 1905, i, 934).

The green salt obtained by Wieland by the action of ethereal hydrogen chloride on di-*p*-tolyldihydrotolazine is more readily prepared by the oxidation of di-*p*-tolylamine with sodium dichromate in acetic acid solution and treating the product with hydrochloric acid. It has the composition $C_{56}H_{54}N_4Cl_4$ and is a *N*-quinhydrone, consisting of di-*p*-tolyltolazonium dichloride (1 mol.) combined with di-*p*-tolyldihydrotolazine dihydrochloride (1 mol.); on crystallisation from water it loses 2HCl, yielding the normal salt, $C_{56}H_{52}N_4Cl_2$. The quinhydrone salts are converted by aqueous ferric chloride into the *holo* quinonoid salt, which was isolated in the form of its dark brown *platinichloride*, $C_{28}H_{26}N_2PtCl_6$.

Oxidation of diphenylamine by means of potassium persulphate and sulphuric acid in glacial acetic acid solution at the ordinary temperature yields the N-*quinhydrone sulphate* of NN'-*diphenylbenzidine*. This is a dark olive-green, microcrystalline substance, which is oxidised by excess of potassium persulphate, or better by sodium dichromate and sulphuric acid, to the corresponding *holo*-quinonoid *sulphate*.

When decomposed by water, the dark blue liquid formed by the addition of sodium nitrite to a solution of diphenylamine in strong sulphuric acid yields an olive-green precipitate, which contains the following substances: (1) the *N*-quinhydrone sulphate of *NN'*-diphenylbenzidine. (2) *Di*-p-*nitroso*-N:N'-*diphenylbenzidine*,

$$NO{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NO,$$

which forms yellowish-red granules (decomp. 290°), gives a violet-red coloration with sulphuric acid, and is often accompanied by *NN'*-diphenylbenzidine, from which it is separated only with difficulty.

NN'-*Diphenylbenzidinedinitrosoamine*,

$$NO\cdot NPh\cdot C_6H_4\cdot C_6H_4\cdot NPh\cdot NO,$$

which forms microscopic, yellowish-white needles, m. p. 124°, and dissolves in strong sulphuric acid with a blue coloration and evolution of nitric oxide. From the instability of the dinitrosoamine in sulphuric acid, the authors draw the conclusion that the original blue solution, obtained by the addition of sodium nitrite to diphenylamine in sulphuric acid, contains *NN'*-diphenylbenzidine, and that the formation of the dinitrosoamine takes place during the subsequent dilution with water. The addition of sodium nitrite to a solution of *NN'*-diphenylbenzidine in glacial acetic acid, containing a little sulphuric acid at the ordinary temperature, yields the above-mentioned dinitrosoamine; if the mixture is warmed, di-p-nitroso-*NN'*-diphenylbenzidine is produced; in one instance, using an excess of sodium nitrite, a *nitrosoamine* of the last-mentioned compound,

$$NO\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N(NO)\cdot C_6H_4\cdot NO,$$

was obtained.

Oxidation with ferric chloride and a mixture of acetic and sulphuric acids converts *NN'*-diphenylbenzidine into a dark green *N*-quinhydrone salt, from which the blue *holo*-quinonoid salt,

$$NPh\colon C_6H_4\colon C_6H_4\colon NPh,HCl,$$

is obtained by oxidation with chromic acid. The dark violet crystalline *platinichloride* of the *holo*-quinonoid salt,

$$(C_{24}H_{18}N_2Cl)_2PtCl_4,5H_2O,$$

was analysed. F. B.

δ-Phenyl-α-methyltetramethylenediamine. [αδ-Diamino-α-phenylpentane.] CESARE FINZI (*Gazzetta*, 1912, 42, ii, 364—367).—Acetophenoneacetonedioxime is best obtained by the action of hydroxylamine hydrochloride on an excess of the monoxime (compare this vol., i, 995) in alkaline solution. When the dioxime is reduced with sodium and alcohol, *αδ-diamino-α-phenylpentane* is obtained. It is a dense, yellow oil, which absorbs carbon dioxide from the air, and gives the reactions and precipitates characteristic of alkaloids. Its *carbonate* (or *carbamate*) decomposes at 90—100°. The *platinichloride*,

$$C_{11}H_{18}N_2,H_2PtCl_6,$$

crystallises in tufts of yellow needles, which become brown at 245° and melt at 249° (decomp.). The *dibenzoyl* derivative, $C_{25}H_{26}O_2N_2$, has m. p. 224°. R. V. S.

Preparation of Pyrazolone Derivatives in the Benzene Series Containing a Free Hydroxyl Group. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249626).—Pyrazolones containing a free hydroxyl group are of technical importance for the preparation of dyes and pharmaceutical products, and can be prepared by the action of acetoacetic ester on the hydrazines of aminophenols.

1 : 2'-*Hydroxy-5'-sulphophenyl-3-methyl-5-pyrazolone*,

$$SO_3H\cdot C_6H_3(OH)\cdot N{<}{\begin{matrix}N\colon CHMe\\ CO\cdot CH_2\end{matrix}},$$

colourless crystals, is obtained as follows: 2-amino-*p*-phenolsulphonic acid is diazotised, reduced to 2-*hydrazino*-p-*phenolsulphonic acid*, which

is then treated with ethyl acetoacetate in concentrated aqueous solution, when, after prolonged stirring at 60°, the ring closes and furnishes the foregoing compound.

1 : 3′ : 5′-*Dichloro-2′-hydroxyphenyl-3-methyl-5-pyrazolone*,

$$OH\cdot C_6H_2Cl_2\cdot N\!<\!\begin{matrix}N{=}CMe\\ \vert\\ CO\cdot CH_2\end{matrix},$$

is prepared in a similar manner from 4 : 6-dichloro-*o*-aminophenol, whilst 4-chloro-2-amino-*o*-phenolsulphonic acid furnishes 1 : 5′-*chloro-2′-hydroxy-3′-sulphophenyl-3-methyl-5-pyrazolone*,

$$SO_2H\cdot C_6H_2Cl(OH)\cdot N\!<\!\begin{matrix}N{=}CMe\\ \vert\\ CO\cdot CH_2\end{matrix},$$

when the intermediate *hydrazine* is treated with acetoacetate, or if ethyl-oxalacetate is employed it yields 1 : 5′-*chloro-3′-sulpho-2′-hydroxyphenyl-5-pyrazolone-3-carboxylic acid*, $SO_3H\cdot C_6H_2Cl(OH)\cdot N\!<\!\begin{matrix}N{=}C\cdot CO_2H\\ \vert\\ CO\cdot CH_2\end{matrix}$, or with sodium dioxytartrate it furnishes a red tartrazine dye.

Other aminophenols and their derivatives (Abstr., 1908, i, 785) can be employed in this reaction. F. M. G. M.

Derivatives of 5-Benzylpyrimidine. HERMANN KAST (*Ber.*, 1912, **45**, 3124—3135).—Benzylbarbituric acid is best prepared by condensing ethyl benzylmalonate with carbamide by means of sodium ethoxide in alcoholic solution. It is converted by phosphoryl chloride at 120° into 2 : 4 : 6-*trichloro-5-benzylpyrimidine*, which crystallises in colourless needles, m. p. 66·5°, and when warmed with hydriodic acid and phosphonium iodide yields 2(or 6)-*iodo-4-hydroxy-5-benzylpyrimidine*. This forms long, colourless needles, m. p. 208°, dissolves in both acids and alkalis, and has also been prepared by the action of hydriodic acid on 2 : 6-*dichloro-4-methoxy-5-benzylpyrimidine*, which crystallises in colourless prisms, m. p. 74°, and is readily obtained by the interaction of 2 : 4 : 6-*trichloro-5-benzylpyrimidine* and sodium methoxide in methyl-alcoholic solution.

2 : 6-Dichloro-4-methoxy-5-benzylpyrimidine reacts with alcoholic ammonia, yielding 6-*chloro-2-amino-4-methoxy-5-benzylpyrimidine*, colourless platelets, m. p. 162°, and with methyl-alcoholic sodium methoxide to form 6-*chloro-2 : 4-dimethoxy-5-benzylpyrimidine*, which separates from alcohol in rhombohedric crystals, m. p. 48°, belonging to the triclinic system, and, on reduction with zinc and hydrochloric acid in alcoholic solution, is converted into 2 : 4-*dihydroxy-5-benzylpyrimidine* (*phenylthymine*). This forms small, prismatic crystals, m. p. 285—286°, and may be obtained directly from benzylbarbituric acid by reduction with phosphorus and hydriodic acid at 150—160°.

2 : 4 : 6-*Trimethoxy-5-benzylpyrimidine*, prepared from 2 : 4 : 6-trichloro-5-benzylpyrimidine and excess of sodium methoxide, has m. p. 99·5°.

The trichloro-compound reacts with ammonia at the ordinary temperature, yielding 4 : 6-*dichloro-2-amino-5-benzylpyrimidine*, which crystallises in needles, m. p. 204·5°, and is accompanied by 2 : 4-*dichloro-6-amino-5-benzylpyrimidine*. The last-mentioned compound

cry[illegible]llises with benzene ($\frac{1}{2}$ mol.), which is lost at 100°; from alcohol it [illegible]parates in long, slender, lustrous, silky needles.

[illegible]he constitution of 4 : 6-dichloro-2-amino-5-benzylpyrimidine has b[illegible]en established by its synthesis from *benzylmalonylguanidine*,

$$NH_2\cdot C{<}{\begin{matrix}N{-}CO\\NH\cdot CO\end{matrix}}{>}CH\cdot C_7H_7.$$

This crystallises with $1H_2O$, and is prepared by the condensation of ethyl benzylmalonate and guanidine thiocyanate with sodium ethoxide in alcoholic solution; when heated at 120—125° with phosphoryl chloride, it yields 4 : 6-dichloro-2-amino-5-benzylpyrimidine, which is reduced by zinc dust and aqueous alcohol to 2-*amino*-5-*benzylpyrimidine*, crystallising in lustrous scales, m. p. 133·5° (*aurichloride*, yellow needles; *platinichloride*, orange-red needles).

The action of methyl-alcoholic ammonia on 4 : 6-dichloro-2-amino-5-benzylpyrimidine leads to the formation of 6-chloro-2-amino-4-methoxy-5-benzylpyrimidine.

2- or 6-*Iodo*-4-*amino*-5-*benzylpyrimidine*, prepared by reducing 2 : 6-dichloro-4-amino-5-benzylpyrimidine with hydriodic acid and phosphonium iodide, crystallises in columns, m. p. 201°; the *hydrochloride*, rhombohedra, *hydriodide*, *aurichloride*, and *platinichloride* are described. On reduction with zinc dust and aqueous alcohol, it yields 4-*amino*-5-*benzylpyrimidine*, which crystallises in lustrous, colourless platelets, m. p. 156°, and forms a *zinci-iodide* crystallising in short, flat needles, m. p. about 240°.

2 : 4 : 6-Trichloro-5-benzylpyrimidine reacts with alcoholic ammonia at 150—160° to form 6-*chloro*-2 : 4-*diamino*-5-*benzylpyrimidine*. This crystallises in white needles, m. p. 163°, and has also been obtained by the reaction of 4 : 6-*dichloro*-2-*amino*-5-*benzylpyrimidine* with ammonia in alcoholic solution. When reduced with zinc and hydrochloric acid in aqueous solution, 6-chloro-2 : 4-diamino-5-benzylpyrimidine is converted into 2 : 4-*diamino*-5-*benzylpyrimidine*, which forms small, felted needles, melting at 145—146°, to a turbid liquid.

Reduction with hydriodic acid and phosphonium iodide yields 6-*iodo*-2 : 4-*diamino*-5-*benzylpyrimidine hydriodide*, pale yellow, pointed needles, m. p. 246—250° (decomp.), from which the free *base* is liberated by aqueous alkalis. This crystallises in clusters of needles, which become brown and have m. p. 191—192°; the *hydrochloride* is mentioned. On reduction with zinc and aqueous alcohol, it gives rise to 2 : 4-diamino-5-benzylpyrimidine. F. B.

Preparation of Derivatives of Barbituric Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247952. Compare Trans., 1909, **95**, 979).—5-*Phenyl*-5-*ethylbarbituric acid*, $CO{<}{\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}}{>}CEtPh$, leaflets, m. p. 170°, is prepared by boiling 264 parts of *ethyl phenylethylmalonate* (b. p. 166°/12 mm.) with sodium (69 parts) and carbamide (90 parts) in absolute alcoholic solution during six hours and evaporating the filtered solution in a vacuum with the addition of dilute hydrochloric acid until the liquid is only feebly alkaline; it furnishes crystalline *calcium* and *sodium* salts.

5-*Phenyl*-5-*benzylbarbituric acid*, m. p. 235° ; 5-*phen*[illegible] 5-[illegible]*hyl-barbituric acid*, m. p. 220° ; 5-*phenyl*-5-*propylbarbituric* *acid*, [illegible] p. 190° ; and 5-p-*methoxyphenyl*-5-*ethylbarbituric acid*, m. p. [illegible] [illegible]re also described in the original. F. M. G. [illegible]

Preparation of Derivatives of Barbituric Acid. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D R.-P. 249722. Compare following abstract).—*Phenylethylmalonyl chloride*, b. p. 50—60°/15 mm., is prepared from phenylethylmalonyl ester by hydrolysis with alcoholic sodium hydroxide at the ordinary temperature ; the *phenylethylmalonic acid* (m. p. 155°) so obtained is then converted into its chloride by the usual method ; when the foregoing chloride is condensed with methyl-*iso*carbamide hydrochloride in benzene solution, it furnishes 2-*methoxy*-5-*phenyl*-5-*ethylbarbituric acid*, $OMe\cdot C{<}\begin{smallmatrix}N—CO\\ NH\cdot CO\end{smallmatrix}{>}CEtPh$, m. p. 152°; this when warmed with 30% hydrochloric acid evolves methyl chloride and yields phenylethylbarbituric acid, $\begin{smallmatrix}N—CO\cdot CEtPh\\ \| \qquad\quad | \\ OMe\cdot C\cdot NH\cdot CO\end{smallmatrix}$, m. p. 170°.

Benzylmalonyl chloride has b. p.141°/15 mm., and when condensed with ethyl*iso*carbamide hydrochloride furnishes 2-*ethoxy*-5-*benzylbarbituric acid*, $OEt\cdot C{<}\begin{smallmatrix}N—CO\\ NH\cdot CO\end{smallmatrix}{>}C\cdot CH_2Ph$, m. p. 202°, which when treated with 45% hydrobromic acid yields benzylbarbituric acid, m. p. 206°.

2-*Ethoxy*-5-*phenylbarbituric acid*, $OEt\cdot C{<}\begin{smallmatrix}N—CO\\ NH\cdot CO\end{smallmatrix}{>}CHPh$, m. p. 218°, is prepared in a similar manner from *phenylmalonyl chloride*, b. p. 122°/15 mm., and on treatment with concentrated sulphuric acid furnishes 5-*phenylbarbituric acid*, m. p. 250°. F. M G. M.

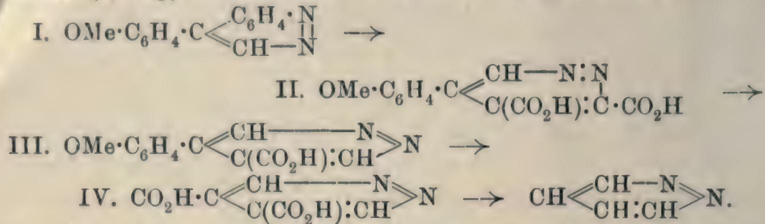
Preparation of Mono- and Di-alkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249907. Compare Abstr., 1900, i, 340, 431, and preceding abstract).—The action of mono- or di-alkylmalonyl haloids on *iso*carbamide ethers furnishes barbituric acids of general formula $OR\cdot C{<}\begin{smallmatrix}N—CO\\ NH\cdot CO\end{smallmatrix}{>}CR^1R^2$ (where R is alkyl, R^1 hydrogen or alkyl, and R^2 alkyl), which when treated with mineral acids yield alkylbarbituric acids.

2-*Methoxy*-5:5-*diethylbarbituric acid*, $OMe\cdot C{<}\begin{smallmatrix}N—CO\\ NH\cdot CO\end{smallmatrix}{>}CEt_2$, m. p. 131°, is prepared from diethylmalonyl chloride and methyl*iso*carbamide hydrochloride, $OMe\cdot C:NH(NH_2)$, in aqueous-benzene solution in the presence of sodium hydroxide ; when warmed with 30% hydrochloric acid it furnishes 5 : 5-diethylbarbituric acid and methyl chloride.

2-*Ethoxy*-5-*ethylbarbituric acid*, $OEt\cdot C{<}\begin{smallmatrix}N—CO\\ NH\cdot CO\end{smallmatrix}{>}CHEt$, m. p. 211°, is obtained from ethyl*iso*carbamide hydrochloride and ethylmalonyl chloride ; it is decomposed by boiling hydrobromic acid into 5 : 5-ethylbarbituric acid. F. M. G. M.

Cinnoline Syntheses. 4-Anisylcinnoline. RICHARD STOERMER and O. GAUS (*Ber.*, 1912, 45, 3104—3113).—That the synthesis of

cinnoline derivatives from *o*-amino-*as*-diarylethylenes takes place according to the scheme given previously (Abstr., 1909, i, 841) has already been rendered probable by the transformation of 4-phenylcinnoline into 4-phenylpyridazine. All doubt as to the constitution of the cinnolines has now been removed by the degradation of 4-*p*-anisylcinnoline (I) to pyridazine as shown in the following scheme:



Further, the results obtained with 4-anisylcinnoline confirm the assumption made by Stoermer and Fincke (*loc. cit.*), that the removal of carbon dioxide from the cinnolinic acids takes place in the same manner as in the case of the dibasic acids of the pyridine series, namely, from the carboxyl adjacent to the nitrogen atom.

2-*Amino-4'-hydroxybenzophenone*, prepared by heating 2-amino-4'-methoxybenzophenone (Ullmann and Bleier, Abstr., 1903, i, 176) with hydrobromic acid, crystallises in colourless needles, m. p. 165°, dissolves in both acids and bases with a yellow colour, and reacts with magnesium methyl bromide, yielding *α-o-aminophenyl-α-p-anisylethyl alcohol*, $NH_2\cdot C_6H_4\cdot CMe(OH)\cdot C_6H_4\cdot OMe$, which forms large, light yellow crystals, m. p. 99°, and is converted by boiling for one hour with 10% sulphuric acid into *o-aminophenyl-p-anisylethylene*,

$$NH_2\cdot C_6H_4\cdot C(C_6H_4\cdot OMe):CH_2.$$

This crystallises in colourless needles, m. p. 49°, and forms a light yellow *platinichloride*, m. p. 190°. Its solution in hydrochloric acid on treatment with sodium nitrite yields 4-p-*anisylcinnoline* (I), long, pale yellow needles, m. p. 85°, from which the following derivatives were prepared: *hydrochloride*, B,HCl,H_2O, yellow crystals, m. p. 215°; *picrate*, m. p. 150°; *nitrate*, which crystallises in slender, dark yellow needles, m. p. 151—152°, and reacts with silver nitrate in nitric acid or alcoholic solution to form the *compound*, $C_{15}H_{12}ON_2,AgNO_3$, golden-yellow needles, m. p. 250° (decomp.); *sulphate*, B,H_2SO_4, m. p. 211° (decomp.); *methiodide*, long, dark reddish-brown needles (decomp. 220°); *methochloride*, which is light yellow, m. p. 190° (decomp.); *platinichloride*, brownish-yellow crystals (decomp. 200°). It forms with auric chloride in alcoholic solution the *aurichloride*, $2B,2HCl,AuCl_3$, slender, golden-yellow needles (decomp. about 100°); in aqueous hydrochloric acid solution the *normal aurichloride*, $B,HCl,AuCl_3$, m. p. 120° (decomp.), is produced.

4-p-*Hydroxyphenylcinnoline*, $C_{14}H_{10}ON_2$, prepared by heating the anisyl compound with hydrobromic acid, crystallises in pale yellow leaflets, m. p. 230°, and forms a *sulphate*, B,H_2SO_4, light red leaflets, m. p. 210°, and a reddish-yellow *platinichloride* (decomp. 252°); its solutions in aqueous sodium hydroxide have an intensely dark yellow colour, and deposit a canary-yellow, crystalline *sodium* salt, m. p. 85°.

4-Anisylcinnoline is oxidised by potassium permanganate in aq solution to 4-p-*anisylcinnolinic* (*4-anisylpyridazine*-5 : 6-*dicarbox* *acid* (II). This crystallises in slender, white needles, m. p. 205°, c taining $1H_2O$, which cannot be removed without simultaneous loss carbon dioxide and transformation into 4-*p*-anisylpyridazine-5-car oxylic acid ; it forms an *acid silver* salt,

$$C_{13}H_8O_5N_2Ag_2,C_{13}H_9O_5N_2Ag,$$

a *normal silver* salt, $C_{13}H_8O_5N_2Ag_2,H_2O$, and a *barium* salt crystallising in lustrous, white leaflets.

4-p-*Anisylpyridazine-5-carboxylic acid* (III), prepared by heating the preceding compound, forms long, pale yellow needles, m. p. 205°, and yields a *platinichloride*.

When warmed with dilute nitric acid, 4-anisylcinnolinic acid is converted into a *nitro*-derivative of 4-*p*-anisylpyridazine-5-carboxylic acid, $C_{12}H_9O_5N_2$, which crystallises in slender, felted, light yellow needles, m. p. 230° (decomp.), and probably contains the nitro-group in the anisyl residue. On reduction with ferrous sulphate and ammonia, the nitro-compound yields *amino*-p-*anisylpyridazine-5-carboxylic acid*, slender, pale brown needles, m. p. 225° (decomp.).

4-p-*Anisylpyridazine*, $N{<}{\begin{matrix}CH{:}CH\\ N{-}CH\end{matrix}}{>}C{\cdot}C_6H_4{\cdot}OMe$, obtained by the distillation of 4-*p*-anisylpyridazine-5-carboxylic acid with soda-lime under diminished pressure, forms almost colourless, long needles, m. p. 85°, and when heated with hydrobromic acid is transformed into 4-p-*hydroxyphenylpyridazine*, long, colourless needles, m. p. 242°.

4-p-*Hydroxyphenylpyridazine-5-carboxylic acid*, $\begin{matrix}N{\cdot}CH{:}C{\cdot}CO_2H\\ \| \quad\quad\; | \\ N{\cdot}CH{:}C{\cdot}C_6H_4{\cdot}OH\end{matrix}$' prepared by heating 4-*p*-anisylcinnolinic acid with hydrobromic acid, crystallises in dark yellow needles, m. p. 225° (decomp.), containing $1H_2O$, which is lost at 120° ; the anhydrous acid forms long, citron-yellow needles, m. p. 240°, and is best obtained by heating 4-*p*-anisylpyridazine-5-carboxylic acid with hydrobromic acid ; the *silver* salt is a yellow powder.

When oxidised with potassium permanganate in alkaline solution, the preceding compound yields pyridazine-4 : 5-dicarboxylic acid (IV), which becomes brown at 208° (decomp. 209—210°) (compare Täuber, Abstr., 1895, i, 301 ; Gabriel, Abstr., 1904, i, 103), and is converted by loss of carbon dioxide into pyridazine ; the *platinichloride* of the latter base forms slender, yellow needles (decomp. 180°). F. B.

A Red Indigotin, 5 : 5′-Dichloro-4 : 4′-dimethylindigotin. FRANZ KUNCKELL and RICHARD LILLIG (*J. pr. Chem.*, 1912, [ii], 86, 517—518).—2-*Chloroaceto*-p-*toluidide* forms snow-white needles, m. p. 104°, and reacts with chloroacetyl chloride and aluminium chloride in carbon disulphide solution, yielding ω : 4-*dichloro*-6-*acetylamino*-3-*methylacetophenone*, $NHAc{\cdot}C_6H_2MeCl{\cdot}CO{\cdot}CH_2Cl$, which forms yellow crystals, m. p. 163°, and is converted by boiling with 5% aqueous sodium hydroxide and simultaneous atmospheric oxidation into a red or reddish-violet 5 : 5-*dichloro*-4 : 4′-*dimethylindigotin*. ω : 4-*Dichloro*-6-*amino*-3-*methylacetophenone* crystallises in yellow needles, m. p. 118°.

F. B.

Behaviour of Phenylazoimide with Aniline and with p-Toluidine. LUDWIG WOLFF (*Annalen*, 1912, 394, 59—68).—Although a diazoketone and phenylazoimide react in an analogous manner with potassium cyanide, their behaviour with aniline is quite dissimilar. Whilst the diazoketone yields an anilide (next page), phenylazoimide and aniline at about 150° yield a *substance*, $C_{12}H_{12}N_2$, m. p. 151°, colourless needles, which is called *dibenzamil*, and to which the constitution $\begin{array}{l}\mathrm{CH{:}CH{\cdot}CH{\cdot}NH} \\ \mathrm{\,|\qquad\quad\ |\quad\ \,|} \\ \mathrm{CH{:}CH{\cdot}CH{\cdot}NPh}\end{array}$ is provisionally ascribed. It forms an *aurichloride*, m. p. 148° (decomp.), yellow prisms, reacts with phenylcarbimide at the ordinary temperature to form a *phenylcarbamide*, $C_{19}H_{17}ON_3$, m. p. 127—128°, glistening prisms, and yields with acetic anhydride at the ordinary temperature an oily *acetyl* derivative, which is converted by heating into *acetyl*-o-*aminodiphenylamine*, $C_{14}H_{14}ON_2$, m. p. 121°, colourless needles. The latter, which is also obtained by acetylating *o*-aminodiphenylamine, is converted by boiling alcoholic sodium hydroxide or by cold hydrochloric acid into 1-*phenyl-2-methylbenziminazole*, $C_6H_4{<}\substack{NPh\\N}{>}CMe$, m. p. 72—73°, colourless prisms. By benzoylation with benzoyl chloride and cold 10% sodium hydroxide, dibenzamil yields a brown, viscous substance and *benzoyl*-o-*aminodiphenylamine*, $NHBz{\cdot}C_6H_4{\cdot}NHPh$, m. p. 136°; from the latter, 1 : 2-*diphenylbenziminazole*, m. p. 111° (*hydrochloride*, m. p. 260° [decomp.]), can be obtained.

[With F. KOLASIUS.]—Phenylazoimide and *p*-toluidine at 140° yield a *substance*, $C_{13}H_{14}N_2$, m. p. 116°, colourless needles, by the benzoylation of which a brown viscous mass is produced, from which benzo-*p*-toluidide is obtained by treatment with alcohol and hydrochloric acid.

C. S.

Preparation of Anthraquinone Derivatives. FRANZ ULLMANN (D.R.-P. 248998. Compare Abstr., 1911, i, 165504).—It is found that the halogenated pyridazoneanthrones condense readily with aromatic amines to form arylaminopyridazoneanthrones.

4-*Anilinopyridazoneanthrone*, orange-red needles, is prepared by boiling *pyridazone*-4-*chloroanthrone* (obtained from hydrazine and 1 : 4-chloroanthraquinonecarbonyl chloride), with aniline (6 parts), potassium acetate (0·4 part), and copper acetate (0·1 part).

4-p-*Toluidinophenylpyridazoneanthrone*, orange needles, m. p. 290°, is obtained in a similar manner from *p*-toluidine and phenylpyridazone-4-chloroanthrone. These compounds can be readily sulphonated, yielding soluble *compounds*, which dye wool yellow shades.

F. M. G. M.

Diazoanhydrides (1 : 2 : 3-Oxadiazoles or Diazo-oxides) and Diazoketones. LUDWIG WOLFF (*Annalen*, 1912, 394, 23—59).—*Phenylglyoxalhydrazone*, $NH_2{\cdot}N{:}CH{\cdot}COPh$, m. p. 120—121°, colourless needles, obtained by passing hydrogen sulphide into a concentrated alcoholic solution of diazoacetophenone containing a few drops of ammonium sulphide, is easily decomposed into acetophenone and nitrogen by heating above its m. p., or by warming with aqueous

sodium hydroxide, reduces Fehling's solution, ferric chloride and mercuric chloride, and is oxidised quantitatively to diazoacetophenone by potassium permanganate. It condenses with *p*-nitrobenzaldehyde in warm alcohol to form *phenylglyoxal*-p-*nitrobenzylideneazine*,

$$NO_2\cdot C_6H_4\cdot CH\colon N\cdot N\colon CH\cdot COPh,$$

m. p. 138°, yellow prisms, and reacts with hot acetic anhydride to form the *acetyl* derivative, $NHAc\cdot N\colon CH\cdot COPh$, m. p. 145—146°, which, unlike the parent substance, has feeble acid properties.

Phenylglyoxalhydrazone instantly reduces an ammoniacal solution of silver oxide, and is itself thereby converted into phenylacetamide. This transformation is due to the conversion of the initially formed diazoacetophenone into the amide by the ammonia, the transformation being catalytically accelerated by the silver oxide. Diazoacetophenone is converted into nitrogen and benzoylcarbinol by boiling water, into phenylacetic acid by a solution of silver oxide in aqueous sodium thiosulphate at 50—60°, into phenylacetamide by a little silver oxide in aqueous ammonia, and into phenylacetanilide by boiling aniline. Similarly, diazoacetone is converted into propionamide by aqueous ammonia containing silver oxide, and into propionanilide by hot aniline.

[With R. Greulich.]—By reduction to aminoacetylacetone and subsequent diazotisation, oximinoacetylacetone is converted into 4-*acetyl*-5-*methyl*-1 : 2 : 3-*oxadiazole* (*diazoacetylacetone anhydride*),

$$O<\begin{matrix}N{=\!=}N\\ \quad | \\ CMe\colon CAc'\end{matrix}$$

a yellow oil, which yields *diazoacetone*, $CH_3\cdot CO\cdot CH\colon N_2$, b. p. 4—47°/15 mm., by treatment with dilute sodium hydroxide at 0°. Diazoacetone is a pale yellow, not unpleasantly odorous liquid, D^0 1·0864, which is converted into acetylcarbinol and nitrogen by water at 70—80°, into *diazoacetone cyanide*, $CH_3\cdot CO\cdot CH_2\cdot N\colon N\cdot CN$ (*semicarbazone*, m. p. about 210° [decomp.], yellow, crystalline powder), by concentrated aqueous potassium cyanide, and into *di-iodoacetone*,

$$CH_3\cdot CO\cdot CHI_2,$$

by iodine in chloroform at 30°. A concentrated solution of di-iodoacetone in chloroform yields iodine and methylglyoxal by prolonged exposure to air in diffused daylight.

The diazoanhydride of ethyl acetoacetate and boiling aniline yield ethyl *iso*succinanilate ; the diazo-anhydride of acetylacetone and aniline at 100° yield methylacetoacetanilide ; the 4-benzoyl-5-methyl-1 : 2 : 3-oxadiazole and aniline at 85—100° yield *a-benzoylpropionanilide*, $CHMeBz\cdot CO\cdot NHPh$, m. p. 137—138°, colourless prisms, and *a-acetylphenylacetanilide*, $CHPhAc\cdot CO\cdot NHPh$, m. p. 97°, colourless needles. The preceding reactions can be explained by assuming that the diazo-anhydride changes to the diazo-ketone ; this loses nitrogen and leaves a complex which yields by migration of a radicle a keten to which the aniline adds to yield the final product or products:

$$R\cdot CO\cdot C<\begin{matrix}CR'\cdot O\\ \quad | \\ N{=\!=}N\end{matrix} \longrightarrow R\cdot CO\cdot C(\colon N_2)\cdot COR' \longrightarrow R\cdot CO\cdot \dot{\underset{\cdot}{C}}\cdot COR' \longrightarrow$$

$$R\cdot CO\cdot CR'\colon CO \text{ or } CO\colon CR\cdot COR'.$$

[With R. Krüche.]—In the presence of acetic acid, the preceding

subst[ance]s react in a different manner, and yield 1 : 2 : 3-triazoles: $R\cdot CO\cdot C{<}\begin{matrix}CR'\cdot O\\ N{=}N\end{matrix} + NH_2R'' \longrightarrow R\cdot CO\cdot C{<}\begin{matrix}CR'\cdot NR''\\ N{=}N\end{matrix}$. The following su[bst]ances have been obtained by the interaction of a primary base a[nd] the diazo-anhydride of ethylacetoacetate in acetic acid at 80—100°, a[nd] hydrolysis and decomposition of the product.

5-*Methyl*-1-*ethyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*,

$$CO_2H\cdot C{<}\begin{matrix}CMe\cdot NEt\\ N{=}N\end{matrix},$$

m. p. 184°, colourless prisms, yields by heating 5-*methyl*-1-*ethyltriazole*, b. p. 251°/741 mm.; by oxidation by potassium permanganate, the latter is converted into 1-*ethyltriazole*-5-*carboxylic acid*, m. p. 178—182° (decomp.), from which 1-*ethyltriazole*, b. p. 238—239°, is obtained at its m. p. 1-*Ethyltriazole*-4 : 5-*dicarboxylic acid*, m. p. about 108—110° (decomp.), obtained by oxidising 5-methyl-1-ethyltriazole-4-carboxylic acid, forms crystals containing H_2O. 1 : 5-*Dimethyl*-1 : 2 : 3-*triazole* 4-*carboxylic acid*, $C_5H_7O_2N_3,H_2O$, m. p. about 203° (decomp.), colourless leaflets, yields 1 : 5-*dimethyltriazole*, b. p. 255°, by heating; the base forms a deliquescent *methiodide* and an *aurichloride*, m. p. 149—150°, yellow needles, and yields 1-*methyltriazole*-5-*carboxylic acid*, decomp. 188°, colourless plates, by oxidation with alkaline potassium permanganate at 90°. 1-*Methyltriazole* has m. p. 15—16°, and b. p. 228°.

1-*Benzyl*-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, $C_{11}H_{11}O_2N_3,H_2O$, colourless leaflets, forms an *ethyl* ester, m. p. 79—80°. At its m. p., 168—169°, the anhydrous acid is converted into 1-*benzyl*-5-*methyltriazole*, m. p. 84°, b. p. 325—330°/750 mm.. 1-*Benzyltriazole*-5-*carboxylic acid* has m. p. 196—197° (decomp.).

The decomposition of the acetylmethyloxadiazole by ammonia yields, in addition to diazoacetone, 4-*acetyl*-5-*methyl*-1 : 2 : 3-*triazole*, m. p. 172°, which is readily soluble in aqueous sodium carbonate. C. S.

Colour Bases of the Triphenylmethane Group. Victor Villiger and Eduard Kopetschni (*Ber.*, 1912, **45**, 2910—2922).—The employment of ammonia for the purpose of liberating the colour bases from salts of the triphenylmethane series leads to the production of amines instead of carbinols. These amine bases are colourless, generally well-crystallised compounds which in solubility and m. p. closely resemble the corresponding carbinols. They can be boiled for a short time with alcoholic sodium hydroxide without losing ammonia. Acids transform them into the corresponding dyes:

$$CR_3\cdot NH_2 + 2HCl = CR_3Cl + NH_4Cl.$$

The readiest method of estimating the ammonia removable by acids consists in treating the amine with boiling methyl or ethyl alcohol, whereby the ammonia is quantitatively removed, alkyl ethers of the corresponding carbinols being formed. Perfectly neutral alcohol is, however, incapable of bringing about the change, the presence of a trace of acid being essential.

Tetramethyldi-p-*aminotriphenylmethylamine* is best obtained by extracting a solution of Victoria-green in aqueous hydrochloric acid

with chloroform and subsequent treatment of the dry chloroform extract with gaseous ammonia. The use of aqueous ammonia results in admixture of the amine with more or less carbinol. It has m. p. 138°. When heated for some time at about 110°, it decomposes with evolution of ammonia and methylamine. Boiling, faintly acid ethyl alcohol transforms it quantitatively into the corresponding ethyl ether, m. p. 162—163°.

Phenyltetramethyldi-p-*aminotriphenylmethylamine*, prisms, m. p. 187—195° (decomp.) according to the rate of heating, may be prepared by treating a solution of Victoria-green in pyridine with excess of aniline, or, better, by heating the methyl ether of tetramethyl-*p*-diaminotriphenylcarbinol with aniline during two to three hours at 135—145°. The aniline removable by acid may be estimated by boiling the substance in feebly acid alcoholic solution, and subsequent distillation of the aniline in steam and titration of it by means of *N*/10-sodium nitrite.

Tetramethyldi-*p*-aminotriphenylcarbinol is obtained by the gradual addition of sodium hydroxide to an aqueous solution of Victoria-green. It separates from light petroleum in indistinct crystals, m. p. 120—122°, and from ether in microscopic cubes, m. p. 109—110°. Solutions of it in toluene or xylene deposit large quadratic plates or cubes, m. p. about 109°, which, however, obstinately retain traces of the solvent. Apparently, this is a case of dimorphism, since the crystals of m. p. 120—122° can be transformed into those of m. p. 109—110° by crystallisation from ether, whilst the m. p. of the latter can be raised to 120—122° by crystallisation from light petroleum. The compounds described by O. Fischer (Abstr., 1881, 587) and by Doebner (Abstr., 1883, 861) appear to have been impure.

Hexamethyltri-p-*aminotriphenylmethylamine*, leaflets, m. p. 190—195° (decomp.), is obtained by treating a solution of crystal-violet in chloroform with gaseous ammonia. Feebly acid ethyl alcohol transforms it into the corresponding ethyl ether, m. p. 143° (compare Rosenstiehl, Abstr., 1895, i, 377). The carbinol decomposes at 205—210° (compare Wichelhaus, Abstr., 1886, 362).

Tri-p-*aminotriphenylmethylamine*, which does not melt, is prepared by grinding para-magenta with aqueous ammonia (20%), or, better, by pouring a concentrated solution of the same substance in methyl alcohol into saturated methyl-alcoholic ammonia. Weakly acid methyl alcohol converts it into the corresponding methyl ether (compare Baeyer and Villiger, Abstr., 1904, i, 786).

The amine bases of the triphenylmethane dyes show a close analogy to leucoauramine; thus, the latter when heated with weakly acid ethyl alcohol evolves ammonia, and leaves an oil which is transformed by dilute hydrochloric acid into tetramethyldiaminobenzhydrol, m. p. 102°. When ethyl alcohol is replaced by methyl alcohol, methoxytetramethyldiaminodiphenylmethane, m. p. 71—72°, is produced. The reverse transformation of the hydrol into the amine was also attempted. Tetramethyldiaminobenzhydrol picrate when treated with ammonia in aqueous or methyl-alcoholic solution

yielded, however, the imine, $NH[CH(C_6H_4\cdot NMe_2)_2]_2$, m. p. 188° (Weil, Abstr., 1894, i, 419 gives 185°). H. W.

Pyrimidines and the Reactions of Amidines with Ethyl Acetoacetate. PETER J. SCHESTAKOFF and N. KAZAKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1312—1320).—According to Pinner (Abstr., 1893, i, 735), the synthesis of pyrimidines by the interaction of amidines and ethers of β-ketonic acids (or, in general, β diketones) fails in the case of formamidine, in which the amidine group is united, not with carbon, but with hydrogen; the compound formed in the latter instance was regarded by Pinner as ethyl β-cyanocrotonate.

Guanidine also reacts with β-diketones, yielding pyrimidine derivatives, but it has not been established whether the two amino-groups or one amino- and one imino-group of the guanidine molecule take part in the ring-formation. In order to settle this point, the authors have investigated the interaction of ethyl acetoacetate and 3-methylpyrazolone-1-carbamidine (see below). If the residue,

$$\begin{matrix} CMe{:}N- \\ | \\ CH_2\cdot CO \end{matrix}\!\!>\!N\cdot,$$

is indicated by Pz, the course of this reaction is expressed by the equations: (1) $NH_2\cdot CPz{:}NH + CH_2Ac\cdot CO_2Et =$

$$NH_3 + NH_2\cdot CPz{:}CAc\cdot CO_2Et,$$

and (2) $$\begin{matrix} Pz\cdot C = C\cdot CO_2Et \\ NH_2 \;\; CO\cdot CH_3 \end{matrix} = H_2O + \begin{matrix} Pz\cdot C = C\cdot CO_2Et \\ N = CMe \end{matrix}.$$

(compare Dains, Abstr., 1902, i, 602). The interaction of formamidine and ethyl acetoacetate probably proceeds similarly, the compound described by Pinner as ethyl β-cyanocrotonate having the structure

$$N\!\!<\!\!\begin{matrix} -CH \\ CMe \end{matrix}\!\!>\!C\cdot CO_2Et.$$

Hence, β-keto-acids react to form pyrimidines only with amidines containing in the molecule the complex $C-C(NH_2){:}NH$, amidines in which the carbon atom of the amidine group is united, not with carbon, but with hydrogen or nitrogen, giving derivatives containing the ring $-C\!\!<\!\!\begin{matrix} C \\ N \end{matrix}\!\!>\!C-$.

Further, the above results indicate that the α-modification of 2-amino-6-hydroxy-4-phenylpyrimidine obtained by Warmington (Abstr., 1893, i, 369) from ethyl benzoylacetate and guanidine has the structure: $NH{:}C\!\!<\!\!\begin{matrix} NH\cdot C(OH) \\ N = CPh \end{matrix}\!\!>\!CH$, the β-modification being the tautomeric form $NH_2\cdot C\!\!<\!\!\begin{matrix} N\cdot C(OH) \\ N = CPh \end{matrix}\!\!>\!CH$.

3-*Methylpyrazolone*-1-*carbamidine*, $\begin{matrix} CMe{=}N \\ | \\ CH_2\cdot CO \end{matrix}\!\!>\!N\cdot C(NH_2){:}NH$, prepared by the action of aminoguanidine on ethyl acetoacetate, forms long, colourless needles, m. p. 235° (decomp.), and reduces neither Fehling's solution nor ammoniacal silver solution. With benzaldehyde it yields 3-*methyl*-4-*benzylidenepyrazolone*-1-*carbamidine*,

$$\begin{matrix} CMe{=}N \\ | \\ C({:}CHPh)\cdot CO \end{matrix}\!\!>\!N\cdot C(NH_2){:}NH,$$

which forms orange crystals, m. p. 210° (decomp.). The *oximino*-derivative, $\begin{matrix} CMe{=\!=\!=}N \\ | \\ C(NOH){\cdot}CO \end{matrix}\!\!>\!N{\cdot}C(NH_2){:}NH$, forms pale green crystals, m. p. 222°.

With ethyl acetcacetate, 3-methylpyrazolone-1-carbamidine gives the *compound*, $\begin{matrix} CMe{=}N \\ | \\ CH_2{\cdot}CO \end{matrix}\!\!>\!N{\cdot}C\!\!<\!\!\begin{matrix} C(CO_2Et) \\ \text{———}N \end{matrix}\!\!\gg\!CMe$, which forms colourless or faintly yellow crystals, m. p. 180°, has the normal molecular weight in freezing phenol, gives an intense green coloration, changing to brown on heating, with ferric chloride, and when heated with hydrochloric acid yields carbon dioxide and a colourless *compound*, m. p. 155°. T. H. P.

Preparation of 1-*p*-Dimethylaminophenyl-3 : 4 : 4-trimethyl-5-pyrazolone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 248887).—When 1-phenyl-3 : 4 : 4-trimethyl-5-pyrazolone is nitrated at 0—5° in concentrated sulphuric acid solution, it yields 1-p-*nitrophenyl*-3 : 4 : 4-*trimethyl*-5-*pyrazolone*, spear-shaped crystals, m. p. 126°; this on reduction with tin and hydrochloric acid furnishes 1-p-*amino-phenyl*-3 : 4 : 4-*trimethyl*-5-*pyrazolone*, colourless needles, m. p. 116°, which forms a crystalline *hydrochloride*, and on alkylation is converted into 1-p-*dimethylaminophenyl*-3 : 4 : 4-*trimethyl*-5-*pyrazolone*,

$$NMe_2{\cdot}C_6H_4{\cdot}N\!\!<\!\!\begin{matrix} N{=}CMe \\ \quad | \\ CO{\cdot}CMe_2 \end{matrix},$$

m. p. 58—59°. F. M. G. M.

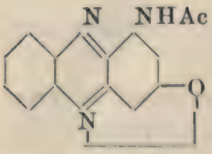
Preparation of Indophenols of the Benziminazole Group and their Leuco-derivatives. ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 248091. Compare Abstr., 1893, i, 433).—When benziminazoles containing an amino-group in the para-position to the imino-group are oxidised together with phenols containing a free para-position they furnish a new series of indophenols.

5-Amino-2-methylbenziminazole (Abstr., 1898, i, 44) when oxidised in the presence of phenol by means of sodium hypochlorite yields an *indophenol* which separates in brownish-red flakes; the leuco-compound obtained by its reduction with sodium sulphide is isolated as a yellow powder.

The analogous *compound* from *o*-cresol is described, and those from other iminazoles and phenolic compounds discussed in the original.

F. M. G. M.

Action of Acetic Anhydride on 1-Amino*apo*safranone. FRIEDRICH KEHRMANN and A. MASSLENIKOFF (*Ber.*, 1912, 45, 2891—2895).—The following behaviour of 1-amino*apo*safranone is in complete harmony with the conception of *apo*safranone as a phenol-betaine. When 1-amino*apo*safranone sulphate is heated with 10 parts of acetic anhydride on the water-bath until the colour has changed to ponceau-red, and the solution is diluted with water and basified with



aqueous ammonia, 1-*acetylaposafranone* (annexed formula), greenish-black crystals with blue reflex, is obtained.

When the preceding sulphate is shaken with acetic anhydride (10 parts) and anhydrous sodium acetate (1 part) at the ordinary temperature until the solution has a magenta colour, and the solution is treated with water and sodium chloride, 1-*amino-3-acetoxy-10-phenylphenazonium chloride*,

$$OAc\cdot C_6H_2(NH_2)\lessgtr{}^{N\text{——}}_{NPhCl}\!>C_6H_4,$$

is obtained as a brownish-violet, crystalline powder, from which 1-amino*apo*safranone is regenerated by aqueous ammonia at the ordinary temperature. By heating 1-acetylamino*apo*safranone with acetic anhydride and sodium acetate on the water-bath until an orange-red solution is obtained, and diluting with water and adding sodium chloride, 1-*acetylamino-3-acetoxy-10-phenylphenazonium chloride* is obtained as a brick-red, crystalline powder; its platinichloride is also a brick-red, crystalline powder. C. S.

Addition of Phenylazoimide to Quinones. LUDWIG WOLFF (*Annalen*, 1912, **394**, 68—85) [with G. K. GRAU].—Approximately equal quantities of *p*-benzoquinone and phenylazoimide react in benzene at 60—65° to yield after twenty-four hours quinhydrone, 4 : 7-*diketo-1-phenyl-1 : 2 : 3-benztriazole*, $\begin{matrix}CH\cdot CO\cdot C\cdot NPh\\ \| \qquad\quad \| \\ CH\cdot CO\cdot C\text{——}N\end{matrix}\!\!>\!N$, m. p. 180—184° (decomp.), golden-yellow leaflets; 4 : 8-*diketo-1 : 5-diphenylbenzditriazole*, $N\lessgtr\begin{matrix}NPh\cdot C\cdot CO\cdot C\text{——}N\\ \| \qquad \| \\ N\text{——}C\cdot CO\cdot C\cdot NPh\end{matrix}\!\!>\!N$, decomp. about 340°, colourless plates; 4 : 8-*diketo-1 : 7-diphenylbenzditriazole*,

$$N\lessgtr\begin{matrix}NPh\cdot C\cdot CO\cdot C\cdot NPh\\ \| \qquad \| \\ N\text{——}C\cdot CO\cdot C\text{——}N\end{matrix}\!\!>\!N,$$

m. p. 280—285° (decomp.), yellow needles, and a yellow *substance*, $C_{18}H_{14}O_2N_4$, m. p. 157°; the last has not been examined further.

4 : 7-Diketo-1-phenyl-1 : 2 : 3-benztriazole is reduced to the corresponding *quinol*, $C_{12}H_9O_2N_3,H_2O$, m. p. 203° (decomp.), colourless needles, by zinc dust and acetic acid, yields 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid by oxidation with sodium hypobromite, forms a *semicarbazone*, $C_{13}H_{10}O_2N_6$, m. p. 247—248° (decomp.), brown needles, and reacts with aniline in warm alcohol to form the *anilino*-derivative, $NHPh\cdot C_6HO_2\lessgtr{}^{NPh}_{\text{—}N}\!\!>\!N$, m. p. 235° decomp.), reddish-brown needles. The anilino-derivative is converted into 6-*hydroxy-4 : 7-diketo-1-phenyl-1 : 2 : 3-benztriazole*, $OH\cdot C_6HO_2\lessgtr{}^{NPh}_{\text{—}N}\!\!>\!N,H_2O$, yellow needles, m. p. about 165—168° (decomp.) when anhydrous, by warm 2% sodium hydroxide, whilst the semicarbazone is converted by boiling 3% sodium hydroxide into ammonia, carbon dioxide, nitrogen, and 7-*hydroxy-1-phenyl-1 : 2 : 3-benztriazole*, $OH\cdot C_6H_3\lessgtr{}^{NPh}_{\text{—}N}\!\!>\!N$, m. p. 234°, almost colourless needles.

4 : 8-Diketo-1 : 5-diphenylbenzditriazole is converted into 1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid by hot 5% sodium hydroxide. 4 : 8-Diketo-1 : 7-diphenylbenzditriazole forms a *semicarbazone*,

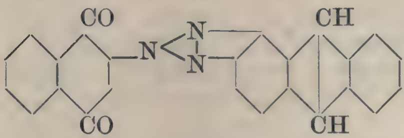
$$C_{19}H_{13}O_2N_9,H_2O,$$

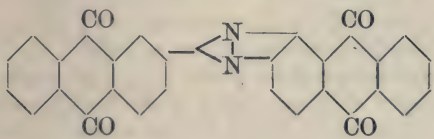
m. p. about 265° (decomp.), yellow needles, and is converted by hot aqueous sodium carbonate, ammonia, or sodium hydroxide into *diphenylditriazole-ketone-5-carboxylic acid*,

$$\begin{array}{l}\mathrm{NPh{\cdot}C(CO_2H)} \\ \mathrm{N{=\!=\!=}N}\end{array}\!\!>\mathrm{C{\cdot}CO{\cdot}C}<\!\!\begin{array}{l}\mathrm{CH{\cdot}NPh,} \\ \mathrm{N{=}N}\end{array}$$

m. p. 230°, colourless needles (*semicarbazone*, $C_{19}H_{15}O_3N_9$, m. p. 234°, colourless needles; *oxime*, $C_{18}H_{13}O_3N_7$, m. p. about 175° [decomp.]), which yields 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid by oxidation with warm alkaline potassium permanganate, and is converted at 200—230° into *diphenylditriazole ketone*, $C_{17}H_{12}ON_6$, m. p. 231°, colourless needles (*oxime*, m. p. 247° [decomp.]). C. S.

[Preparation of Anthraquinone Derivatives.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 250274).—When the *azo*-compound (a dark blue powder) obtained by coupling diazotised 2-aminoanthraquinone with 2-aminoanthracene is oxidised with sodium dichromate in acetic acid solution it furnishes the *compound* (annexed formula), orange-yellow crystals, and on further oxidation in sulphuric acid solution the *compound*:





F. M. G. M.

Preparation of Azo-compounds by Removal of Halogen in the 1 : 6- and 1 : 10-Positions. ROBERT STOLLÉ and FR. SCHMIDT (*Ber.*, 1912, 45, 3116—3123).—The previous work (Abstr., 1911, i, 508) on the formation of azo-compounds by the removal of halogen from the $\alpha:\zeta$-positions has been extended to di-ω-chloro-3 : 6-dibenzhydryl-1 : 2 : 4 : 5-tetrazine (I) and di-ω-chloro-2 : 5-dibenzhydryl-1 : 3 : 4-triazoles of the constitution II (where X = H, p-$C_6H_4{\cdot}OH$, and p-$C_6H_4{\cdot}NMe_2$), but in the latter case the azo-compounds thus produced were too unstable to be isolated.

$$\mathrm{CPh_2Cl{\cdot}C}<\!\!\begin{array}{l}\mathrm{N{\cdot}N} \\ \mathrm{N{:}N}\end{array}\!\!>\mathrm{C{\cdot}CPh_2Cl} \quad \text{(I.)} \qquad \mathrm{CPh_2Cl{\cdot}C}<\!\!\begin{array}{l}\mathrm{N{\cdot}N} \\ \mathrm{NX}\end{array}\!\!>\mathrm{C{\cdot}OPh_3Cl} \quad \text{(II.)}$$

An example of the formation of an azo-compound by the removal of halogen in the $\alpha:\kappa$-positions is also recorded.

1-p-*Hydroxyphenyl*-2 : 5-*dibenzhydryl*-1 : 3 : 4-*triazole* (formula III, X = p-$C_6H_4{\cdot}OH$),

$$\text{(III.)} \quad \mathrm{CHPh_2{\cdot}C}<\!\!\begin{array}{l}\mathrm{N{\cdot}N} \\ \mathrm{NX}\end{array}\!\!>\mathrm{C{\cdot}CHPh_2,}$$

prepared by heating bis-diphenylacetylhydrazide chloride with *p*-aminophenol, forms stout crystals, m. p. 283°, and on chlorination yields a *chloro*-derivative, which gives an intense violet coloration when shaken with mercury in benzene solution.

1-p-*Dimethylamino*-2 : 5-*dibenzhydryl*-1 : 3 : 4-*triazole* (III, X = $p\text{-}C_6H_4\cdot NMe_2$), obtained in a similar manner from *p*-aminodimethylaniline, forms colourless crystals, m. p. 249°, and yields a *chloro*-derivative, m. p. 204° (not sharp) which also gives a violet coloration when its benzene solution is shaken with mercury.

1-*Amino*-2 : 5-*dibenzhydryl*-1 : 3 : 4-*triazole* (III, X = NH_2) is obtained by heating 3 : 6-dibenzhydryl-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine (*loc. cit.*) with alcoholic hydrogen chloride. It crystallises in colourless, felted needles, m. p. 239°, and is accompanied by *s*-bi-diphenylacetylhydrazide.

2 : 5-*Dibenzhydryl*-1 : 3 : 4-*triazole* (III, X = H), prepared by the addition of sodium nitrite to a solution of the preceding compound in alcoholic hydrogen chloride, forms colourless prisms, m. p. 197°, and is also produced, together with a substance, m. p. 212°, by heating bi-diphenylacetylhydrazide chloride with alcoholic ammonia at 80°.

The interaction of diphenylacetyl chloride and 1-amino-2 : 5-dibenzhydryl-1 : 3 : 5-triazole in benzene solution in the presence of pyridine yields 1-*diphenylacetylamino*-2 : 5-*dibenzhydryl*-1 : 3 : 5-*triazole* (III, X = $NH\cdot CO\cdot CHPh_2$), prisms, m. p. 285°, and the corresponding 1-*bi-diphenylacetylamino*-derivative [III, X = $N(CO\cdot CHPh_2)_2$], stout prisms, m. p. 186°.

1-*Diphenylacetylamino*-3 : 6-*dibenzhydryl*-1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*, $\begin{matrix} C(CHPh_2){:}N{-\!\!-}N \\ | \\ NH\cdot N(CO\cdot CHPh_2) \end{matrix}\!\!>\!C\cdot CHPh_2$, obtained from diphenylacetyl chloride and 3 : 6-dibenzhydryl-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine in a similar manner, crystallises in leaflets, m. p. 185°.

Di-ω-chloro-3 : 6-*dibenzhydryl*-1 : 2 : 4 : 5-*tetrazine* (formula I), prepared by chlorinating 3 : 6-dibenzhydryl-1 : 2 : 4 : 5-tetrazine in boiling carbon tetrachloride solution, forms stout, violet-red crystals, m. p. 162° (decomp.), and is slowly converted by boiling in ethyl acetate solution into tetraphenylsuccinonitrile. When shaken with mercury in benzene solution it forms 3 : 6-*bi-diphenylmethylene*-3 : 6-*dihydro*-1 : 2 : 4 : 5-*tetrazine*, $CPh_2{:}C\!<\!\begin{matrix} N{:}N \\ N{:}N \end{matrix}\!>\!C{:}CPh_2$. The latter compound crystallises in black prisms, having a metallic lustre, and explodes at about 170° when rapidly heated. On reduction with zinc and acetic acid it yields 3 : 6-dibenzhydryldihydro-1 : 2 : 4 : 5-tetrazine. It combines with chlorine to form the original dichlorotetrazine, and with bromine, yielding *di-ω-bromo*-3 : 6-*dibenzhydryl*-1 : 2 : 4 : 5-*tetrazine*, m. p. 162°. When heated either alone at 170° or in benzene solution, it loses nitrogen with the formation of tetraphenylsuccinonitrile.

Diphenylacetylhydrazide, $CHPh_2\cdot CO\cdot NH\cdot NH_2$, prepared by heating ethyl diphenylacetate with hydrazine hydrate, crystallises in prisms, m. p. 135°, and is converted by the action of ethyl oxalate at 140—170° into *ββ'-bi-diphenylacetyloxalylhydrazide*,

$$C_2O_2(NH\cdot NH\cdot CO\cdot CHPh_2)_2,$$

which crystallises in slender needles, m. p. 315°, and when heated with

phosphoryl chloride yields 5 : 5′-*dibenzhydryl*-2 : 2′-*bis*-1 : 3 : 4-*oxadiazole*, $CHPh_2 \cdot C \lessgtr \overset{N \cdot N}{\underset{-O-}{}} \gtrless C \cdot C \lessgtr \overset{N \cdot N}{\underset{-O-}{}} \gtrless C \cdot CHPh_2$, colourless needles, m. p. 235°. On chlorination in boiling carbon tetrachloride solution, this gives rise to *di-ω-chloro*-5 : 5′-*dibenzhydryl*-2 : 2′-*bis*-1 : 3 : 4-*oxadiazole*, $CPh_2Cl \cdot C \lessgtr \overset{N \cdot N}{\underset{-O-}{}} \gtrless C \cdot C \lessgtr \overset{N \cdot N}{\underset{-O-}{}} \gtrless C \cdot CPh_2Cl$, m. p. 249°, from which the halogen in the ακ-positions is removed by shaking with mercury in hot xylene solution. The resulting *azo*-compound,

$$CPh_2 \colon C \lessgtr \overset{N \colon N}{\underset{-O-}{}} \gtrless C \colon C \lessgtr \overset{N \colon N}{\underset{-O-}{}} \gtrless C \colon CPh_2,$$

could not be isolated in a state of purity. Its solutions in xylene have an intense emerald-green colour, which disappears when the solutions are exposed to the simultaneous action of air and moisture. Addition of alcohol to the decolorised solutions yields *di-ω-hydroxy*-5 : 5′-*dibenzhydryl*-2 : 2′-*bis*-1 : 3 : 4-*oxadiazole*, m. p. 225—235° (decomp.),

$$OH \cdot CPh_2 \cdot C \lessgtr \overset{N \cdot N}{\underset{-O-}{}} \gtrless C \cdot C \lessgtr \overset{N \cdot N}{\underset{-O-}{}} \gtrless C \cdot CPh_2 \cdot OH.$$

F. B.

Azo-salicylic Acid and Azo-hydroxynaphthoic Acid Dyes. ANUKUL C. SIRCAR and EDWIN R. WATSON (*J. Soc. Chem. Ind.*, 1912, 31, 968—971).—In a previous paper (*ibid.*, 1911, 30, 6) it has been shown that benzeneazosalicylic acid when dyed with a chrome mordant is characterised by a fastness towards light, alkali, and acid, superior to that of any other simple monoazo-dye. Attempts to prepare similar dyes having the same all-round fastness, but of a deeper colour, by replacing the phenyl group with heavier hydrocarbon residues or with other groups containing chromophores, and also by substituting the σ-hydroxynaphthoic acid residue for that of salicylic acid, met with only partial success. Brown and claret-brown shades on chrome-mordanted wool were obtained, but only by the introduction of such groups as are prejudicial to fastness towards milling and light.

m-*Xyleneazosalicylic acid*, $C_6H_3Me_2 \cdot N \colon N \cdot C_6H_3(OH) \cdot CO_2H$, prepared from diazotised *m*-xylidine and salicylic acid, crystallises in orange-yellow needles, m. p. 201°, and forms a *sodium* salt, crystallising in slender, yellow needles.

m-*Xyleneazo-α-hydroxynaphthoic acid*,

$$C_6H_3Me_2 \cdot N \colon N \cdot C_{10}H_5(OH) \cdot CO_2H,$$

forms yellowish-brown needles, m. p. 180°; its *sodium* salt crystallises in brownish-yellow needles.

p-*Ethoxybenzeneazo-α-hydroxynaphthoic acid*,

$$OEt \cdot C_6H_4 \cdot N \colon N \cdot C_{10}H_5(OH) \cdot CO_2H,$$

prepared by coupling *p*-phenetidine with α-hydroxynaphthoic acid, forms yellowish-brown needles, m. p. 198·5°. Diazotised *p*-amino-azobenzene combines with salicylic acid, yielding *benzeneazobenzene*-p-*azosalicylic acid*, $NPh \colon N \cdot C_6H_4 \cdot N \colon N \cdot C_6H_3(OH) \cdot CO_2H$, a yellowish-brown powder, m. p. 248—250°, and with α-hydroxynaphthoic acid to form *benzeneazobenzene*-p-*azo-α-hydroxynaphthoic acid*, m. p. 200—205°.

Benzeneazobenzene-*p*-diazonium chloride (Hewitt and Thole, Trans.,

1910, 97, 514) is obtained in orange prisms by passing nitrous acid into a solution of *p*-aminoazobenzene in alcoholic hydrogen chloride.

Attempts to couple naphthaleneazo-α-naphthalene-4-diazonium sulphate and benzeneazo-α-naphthalene-4-diazonium sulphate with salicylic acid proved unsuccessful.

Diazotised 6 : 8-disulphonaphthalene-2-azo-α-naphthylamine combines with salicylic acid to form 6 : 8-*disulphonaphthalene-2-azo-α-naphthalene-4-azosalicylic acid*, $C_{10}H_5(SO_3H)_2\cdot N\colon N\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_3(OH)\cdot CO_2H$, and with α-hydroxynaphthoic acid, yielding 6 : 8-*disulphonaphthalene-2-azo-α-naphthalene-4-azo-α-hydroxynaphthoic acid*,

$$C_{10}H_5(SO_3H)_2\cdot N\colon N\cdot C_{10}H_6\cdot N\colon N\cdot C_{10}H_5(OH)\cdot CO_2H,$$

which forms a hygroscopic, reddish-brown powder.

Diphenyl-4 : 4′-*bisazo-α-hydroxynaphthoic acid*,

$$C_{12}H_8[N\colon N\cdot C_{10}H_5(OH)\cdot CO_2H]_2,$$

prepared by coupling diazotised benzidine with α-hydroxynaphthoic acid is a brownish-black powder, which does not melt below 275°.

The colorations produced by dissolving the dyes in alkalis and also in strong sulphuric acid together with the shades obtained on unmordanted and chrome-mordanted wool are described. F. B.

The Formation of Lakes between *p*-Nitrobenzeneazo-β-naphthol and Aluminium and Antimony Compounds. ROBERT STREBINGER (*Zeitsch. angew. Chem.*, 1912, 25, 2196—2200).—In alkaline solutions of aluminium sulphate the formation of a lake with *p*-nitrobenzeneazo-β-naphthol, either at room temperatures or at high temperatures, or in the presence of tartaric acid, takes place to such a slight extent, if at all, that it is of no technical importance. There is also practically no lake formation when the above azo-compound is made from a diazotised solution of *p*-nitroaniline and alkaline β-naphthol in the presence of aluminium sulphate. The same results hold when tartar emetic is used in place of aluminium sulphate.

All the preparations obtained in the presence of aluminium sulphate contained traces of SO_4'-anion. T. S. P.

Constitution of Dyes Containing Negative Substituents Derived from Sulphonic Acids of α-Naphthylamine and of α-Naphthol. LUDWIG GATTERMANN and HANS LIEBERMANN (*Annalen*, 1912, 393, 198—214).—Diazotised *p*-chloroaniline, 2 : 5-dichloroaniline, 2 : 4 : 5-trichloroaniline, *o*-, *m*- and *p*-nitroaniline, 4-chloro-3-nitroaniline, 2 : 4-dinitroaniline, sulphanilic acid, and *o*-nitroaniline-*p*-sulphonic acid have been condensed with α-naphthylamine-3- and -5-sulphonic acid in acetic acid solution and with α-naphthol-3- and -5-sulphonic acid in aqueous sodium hydroxide in order to ascertain how the relative amounts of *o*- and *p*-azo-dyes produced in each case are influenced by the presence of the negative substituents.

Those of the preceding amines which are difficultly diazotised by the usual methods are treated as follows. Sodium nitrite (10·6 grams) is added gradually to 180 grams of well cooled, concentrated sulphuric acid, and the mixture is heated at 80° for three to four hours. Eighteen grams of the nitrososulphuric acid (= 1 gram of sodium nitrite), cooled in ice, are stirred and treated rapidly with rather more than the

calculated amount of the amine. If a drop of the solution poured on ice contains nitrous acid, the solution is heated at about 60° for a short time. It is then poured on to ice, the solution of the diazo-sulphate is diluted to about 250 c.c., and filtered from the excess of amine.

The azo-dyes obtained are examined as follows: The washed and dried crude product is decolorised by stannous chloride and hydrochloric acid on the water-bath, the solution is diluted with water, and the naphthylenediaminesulphonic acids or aminonaphtholsulphonic acids are collected and washed, when necessary, with ether to remove the accompanying primary amine.

The solubilities of 1 : 2- and 1 : 4-naphthylenediaminesulphonic acids in aqueous sodium sulphite are so different that they can be quantitatively separated in a mixture of both, and hence the amounts of the ortho- and para-isomerides in the original azo-dye can be calculated. The presence of the 1 : 2-naphthylenediaminesulphonic acide in the mixture of acids obtained can be detected: (i) by the intense green coloration produced by aqueous ferric chloride, and (ii) by the yellow precipitate of sodium naphthaphenanthrazinesulphonate produced by the addition of the sodium hydrogen sulphite compound of phenanthraquinone to a solution of the acids in aqueous sodium acetate faintly acidified with acetic acid. The orientation of the amino-groups in the naphthylenediaminesulphonic acids is determined by replacing the sulphonic acid group by hydrogen by reduction with sodium amalgam and sulphurous acid, and isolating and characterising the resulting naphthylenediamines.

The position of the amino-group in the aminonaphthol-5-sulphonic acids is determined by eliminating the sulpho-group as above. In the case of the aminonaphthol-3-sulphonic acids, however, it is necessary to heat the acids with stannous chloride and concentrated hydrochloric acid at 110° in a sealed tube, whereby 2-amino-1-naphthol-3-sulphonic acid is converted into 2-amino-1-naphthol.

The results of the experiments show that, although a sharp generalisation cannot be made, the presence of the negative substituents in the diazotised amine facilitates in general the formation of the para-azo-dye; thus α-naphthylamine-5-sulphonic acid usually yields a mixture of the ortho- and the para-azo-dyes, the amount of the latter being greater the larger the number and the more strongly negative the character of the substituents in the diazotised amine. The presence of a sulpho-group in the diazotised amine causes abnormal results; thus α-naphthylamine-5-sulphonic acid forms exclusively the ortho-azo-dye with diazotised sulphanilic acid, and exclusively the para-azo-dye with diazotised *o*-nitroaniline-*p*-sulphonic acid.

In general, the naphtholsulphonic acids have a greater tendency than the naphthylaminesulphonic acids to form para-azo-dyes, and the 3-sulphonic acids have a greater tendency than the 5-sulphonic acids to form ortho-azo-dyes. C. S.

Existence of Primary Arylnitrosoamines as well as the Isomeric *anti*-Diazohydrates. ARTHUR HANTZSCH (*Ber.*, 1912, 45, 3036—3040).—Bamberger (this vol., i, 733) has stated that primary

arylnitrosoamines do not exist. The reasons are now summarised for the existence of the primary nitrosoamines as the pseudo-acids corresponding with the *anti*-diazohydrates. They afford the first example of structural isomerism within a purely inorganic complex (N_2OH).

In particular, proof of this individuality is afforded by the fact that the compound $NO_2\cdot C_6H_4\cdot N_2\cdot OH$ shows selective absorption in ethereal solution as the diazohydrate, $NO_2\cdot C_6H_4\cdot N\colon N\cdot OH$, whereas it absorbs generally in chloroform solution as the nitrosoamine, $NO_2\cdot C_6H_4\cdot NH\cdot NO$. Bamberger now accepts this interpretation. E. F. A.

Behaviour of Iron Salts, in the Presence of Albumins and Other Organic Substances, towards Certain Reagents. HENRY J. M. CREIGHTON (*Trans. Nova Scotia Inst. Sci.*, 1912, 13, 61—75).—It has been found that egg-albumin, serum-albumin, and gelatin tend to prevent certain reactions which are exhibited by ferric chloride, potassium ferricyanide, and soluble Prussian-blue under normal circumstances. The same proteins, however, appear to be without influence on the reactions of ferrous ammonium sulphate and potassium ferrocyanide. The activity of the proteins would therefore seem to be confined to tervalent iron.

In regard to the mechanism of inhibition, it is supposed that the tervalent iron salts are adsorbed by the colloidal proteins, and that definite chemical compounds are formed. The complex substances formed are readily decomposed by hydrochloric acid, but are fairly stable towards a rise of temperature. In the case of those which are formed with soluble Prussian-blue, the temperature may be raised to 100° without decomposition setting in.

Apart from the prevention of precipitation on the addition of ammonia or alkali hydroxide to ferric chloride solutions, it has been found that sucrose, glycerol, and tartaric acid have no influence on the behaviour of either ferrous or ferric iron towards different reagents.

H. M. D.

The Intimate Associations of Inorganic Ions with Native and Derived Proteins. DAVID F. HARRIS (*Trans. Nova Scotia Inst. Sci.*, 1912, 13, 76—86. Compare Creighton, preceding abstract).—A number of observations are referred to which show that the functional activity of protoplasm is dependent on the association of the proteins with inorganic substances in a particular and intimate form.

H. M. D.

The Influence of the Physical Condition of Proteins on the Rapidity of their Cleavage by Enzymes. The Importance of Peptic Digestion on the Further Cleavage of Proteins by Trypsin. The Degree of Cleavage of Proteins by Enzymes. EMIL ABDERHALDEN and CHAUNCEY J. VALLETTE PETTIBONE (*Zeitsch. physiol. Chem.*, 1912, 81, 458—472).—The bulk of the paper relates to the methods (optical method, estimation of amino-nitrogen, etc.) which may be employed. Coagulated egg is digested more rapidly

than the fresh material. Pancreatic digestion occurs more rapidly after the preliminary digestion by pepsin has taken place.

W. D. H.

The Free Amino-groups of the Proteins. ALBRECHT KOSSEL and N. GAWRILOW (*Zeitsch. physiol. Chem.*, 1912, 81, 274—279).—Those proteins which lack lysine in their molecule contain no nitrogen which can be titrated in presence of formaldehyde. Proteins containing lysine become acid in presence of formaldehyde. This is confirmed by the titration of a number of proteins with and without lysine. Free proline, which contains an imino-group, can be titrated in presence of formaldehyde, but proteins containing a large proportion of proline show no reaction in presence of formaldehyde. This affords evidence that the nitrogen of proline takes part in the peptide formation, and that the proline nitrogen in these proteins is tertiary.

E. F. A.

Condition which Phosphorus and Calcium Affect in Milk Casein. LÉON LINDET (*Compt. rend.*, 1912, 155, 923—924*).—About one-half of the phosphorus contained in casein, precipitated from milk by rennet, is present as calcium phosphate, the other half being in combination as an organic phosphate, which is easily hydrolysed by weak alkalis in the cold. Three-fifths of the calcium is present as phosphate, and the remaining two-fifths is combined with the acid groups of the casein.

W. G.

Oxyprotosulphonic Acids. II. JOSEF BURACZEWSKI and L. KRAUZE (*Bull. Acad. Sci. Cracow*, 1912, 7 *A*, 698—704. Compare this vol., i, 58).—Attempts have been made to purify and characterise the various fractions of the oxyprotosulphonic acids described previously (this vol., i, 58). Measurements of basicity and of optical activity show little difference, and the same is true of the total sulphur and the amount of sulphur eliminated by lead acetate. The fractions yield iodine derivatives of varying colour and iodine content, but the latter did not exhibit any regularities. The oxidation product obtained on treating the α-fraction with potassium permanganate could be divided into a number of fractions.

E. F. A.

Oxyprotosulphonic Acid from Casein. (Mlle.) M. SCHUBERTHÓWNA (*Bull. Acad. sci. Cracow*, 1912, 7 *A*, 705—713. Compare Buraczewski and Krauze, this vol., i, 58).—The oxyprotosulphonic acids from casein are divisible only into four fractions, the β-fraction crystallising from acetic acid solution in the cold usually failing.

On further oxidation of the α-fraction with potassium permanganate an α'-fraction insoluble in acetic acid was obtained. This is characteristically colourless, whereas the α-fraction from casein is somewhat yellow. It contains about the same proportion of carbon and hydrogen as the α-fraction, but lacks any loosely combined sulphur, and contains less total sulphur. It is also unable to absorb iodine.

No difference in the basicity of the six fractions obtained from casein could be measured, and their optical behaviour was alike. They all contain phosphorus.

E. F. A.

* and *Bull. Soc. chim.*, 1912, [iv], 11, 950—952.

The Influence of Temperature on the Activity of Nuclease. E. C. TEODORESCO (*Compt. rend.*, 1912, **155**, 554—557).—The behaviour of nuclease contained in a fern (*Pteris aquilina*), a lichen (*Avernia prunastri*), and a basidiomycete (*Pholliota mutabilis*) was studied. Equal portions of the fresh material were heated for half an hour to temperatures from 36° to 100°. A solution of sodium nucleate was then added, and the whole incubated at 36° for several days. Temperatures above 66° cause a rapid decrease in activity of the enzyme, whilst 90—100° destroys it. The optimum temperature for the nuclease of *Pholliota* was found to be about 34°. H. B. H.

Preparation of "Lipase Powder" Acting in Neutral Medium and its Technical Application. YOSHIO TANAKA (*J. Coll. Eng. Imp. Univ. Tokyo*, 1912, **5**, 125—136).—"Lipase powder" is an active lipolytic substance, prepared by treating pressed castor seed with acid and completely washing out with water all the soluble matter. The optimum temperature of the digestion in which the zymogen of lipase is most favourably developed is 30—35°. The activity of the liberated lipase depends on the amount and not on the concentration of the acid employed. The length of time of the digestion has little effect on the activity.

Lipase powder is odourless and tasteless. It hydrolyses fats and fatty oils rapidly in absence of any soluble acid, and may be kept for a long time without undergoing appreciable change. N. H. J. M.

Influence of the Products of Change on the Action of Lipase. YOSHIO TANAKA (*J. Coll. Eng. Imp. Univ. Tokyo*, 1912, **5**, 137—141).—The activity of lipase is inhibited by glycerol, and the retardation of the hydrolysis of oils is chiefly due to the glycerol produced, although the reversible action of the lipase is also partly responsible. To obtain the maximum hydrolysis, it is desirable to use the maximum amount of water which does not prevent the production of a good emulsion, or to remove the glycerol and again treat with lipase powder.

Fatty acids are almost without effect on the activity of lipase.

N. H. J. M.

Influence of Some Neutral Salts, Nitrogenous Matters, and Castor Seed Extract on Lipase. YOSHIO TANAKA (*J. Coll. Eng. Imp. Univ. Tokyo*, 1912, **5**, 142—151).—The activity of lipase is much increased by the addition of neutral salts of the alkali metals, and is not retarded in solutions containing as much as 10%. Salts of magnesium, calcium, and especially copper retard the activity of lipase, even in small amounts.

The stimulating effect of salts of the alkali metals and of manganese is only manifested in the first phase of the hydrolysis.

The hydrolysing power of lipase is also increased by adding an extract of castor seed. This is attributed to salts of alkali metals and proteose present in the extract; globulin and other coagulable proteins do not seem to have any effect.

Leucine and asparagine have a distinct stimulating effect on the action of lipase. N. H. J. M.

Action of Lipase on Oxidised and Polymerised Oils. YOSHIO TANAKA (*J. Coll. Eng. Imp. Univ. Tokyo*, 1912, 5, 152—161).—Lipase acts less rapidity on oil oxidised by insolation, or by air alone, than on the original oil, owing probably to the production of substances of greater mol. weight. Rancid oil is also only slowly hydrolysed, owing to the presence of oxidised substances, less readily hydrolysed, and to the retarding effect of the aldehydic substances it contains. Light without air has no effect. Oil which has been heated in an atmosphere of nitrogen is less readily hydrolysed by lipase than the original oil; the polymerised products of glycerides are evidently attacked with difficulty. N. H. J. M.

Paralysis and Stimulation of Zymase and Catalase. HENRI VAN LAER (*Centr. Bakt. Par.*, 1912, ii, 34, 481—484).—The author claims that Lebedeff's maceration method of extracting zymase gives a juice of greater fermentative power than that obtained by Buchner's method. The latter produces a liquid rich in coagulable albumins, and the rate of auto-digestion in such juice has been studied. It was found that an extract of malt retarded auto-digestion, whilst the addition of a solution of papain accelerated the change.

Comparative experiments in which yeast was extracted with water, malt extract, and papain solution show that malt extract increases the activity of zymase and catalase; papain destroys the action of zymase and diminishes that of catalase. H. B. H.

Asymmetric Phosphorus. I. EDGAR WEDEKIND (*Ber.*, 1912, **45**, 2933—2940. Compare Pope and Gibson, Trans., 1912, **101**, 735). —Experiments have been undertaken in the hope of effecting a resolution of an asymmetric phosphonium base into its optically active components. The behaviour of quaternary phosphonium salts towards different solvents has also been examined.

p-Tolyldichlorophosphine was prepared by the action of phosphorus trichloride on toluene in the presence of aluminium chloride (compare Michaelis and Panek, Abstr., 1882, 958), and was transformed by mercury diphenyl into phenyl-*p*-tolylchlorophosphine. The yields are unsatisfactory, but the best results are obtained by use of an excess of the dichloride. An ethereal solution of magnesium ethyl bromide transformed phenyl-*p*-tolylchlorophosphine into phenyl-*p*-tolylethylphosphine (compare Michaelis, Abstr., 1901, i, 300), which, on treatment with methyl iodide, yielded phenyl-*p*-tolylmethylethylphosphonium iodide, m. p. 150° (Michaelis, *loc. cit.*, gives 138°). By treatment with silver *d*-camphorsulphonate in dilute alcoholic solution, the latter substance was converted into *phenyl*-p-*tolylmethylethylphosphonium* d-*camphorsulphonate*, which separated from ethyl acetate in colourless needles, m. p. 128°. Aqueous solutions of this substance rapidly become cloudy, so that for polarimetric observations the addition of a certain amount of alcohol was necessary. In these circumstances, the value $[M]_D + 101·6°$ was observed, whilst in alcohol alone the value $[M]_D + 103·85°$ was obtained. On the supposition that the sulphonate is sufficiently dissociated in dilute aqueous-alcoholic solution, this gives $[M]_D + 52·15°$ for the phosphonium ion. When, however,

the above aqueous-alcoholic solution (10 c.c.) was diluted with water (25 c.c.) and filtered, the molecular rotation diminished from $+103 \cdot 85°$ to $+59 \cdot 89°$.

Phenyl-p-*tolylbenzylethylphosphonium iodide*, m. p. 192°, prepared by the union of phenyl-*p*-tolylethylphosphine with benzyl iodide, was converted into the corresponding d-*camphorsulphonate*. The latter formed a hard, amorphous, glassy mass, which could not be obtained in the crystalline form. The *bromocamphorsulphonate* was also unsuitable for purposes of resolution. *Phenyl*-p-*tolylbenzylethylphosphonium bromide* crystallised in colourless needles, m. p. 215·5°.

Phenyl-*p*-tolylbenzylethylphosphonium iodide was found to be associated in boiling chloroform solution (mol. wt. 728·6, 730. Cal. 416), and also, in contrast to many ammonium and sulphonium salts, to be stable in solution in this reagent. An attempt to electrolyse the fused salt with platinum electrodes was also made. Iodine was formed at the anode. Decomposition occurred at the cathode. Finally, a brown oily residue was obtained, from which hydrochloric acid dissolved a phosphine base which yielded a solid platinichloride.

H. W.

Preparation of 2:5-Diaminophenyl-1-arsinic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 248047).—When 5-nitro-2-aminophenyl-1-arsinic acid, m. p. 235—236° (prepared from *p*-nitroaniline and arsenic acid), is reduced under the following conditions only the nitro-group is attacked, and the $-AsO(OH)_2$ group remains intact, yielding 2:5-*diaminophenyl*-1-*arsinic acid*, needles, decomp. 210°.

5-Nitro-2-aminophenyl-1-arsinic acid (13 parts) is dissolved in 80 parts of 10*N*-sodium hydroxide with 320 parts of water, treated at the ordinary temperature with 110 parts of ferrous chloride solution (18·9% iron), and allowed to remain until the reduction is complete; the solution is filtered, and acidified with sulphuric acid, when the product slowly separates in crystalline form. F. M. G. M.

Preparation of Neutral Readily Soluble Derivatives of 4:4′-Dihydroxy-3:3′-diaminoarsenobenzene. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 249726).—When the therapeutically active diaminodihydroxyarsenobenzenes are treated with formaldehyde bisulphite, they furnish *compounds* which contain the group $CH_2 \cdot SO_3H$, and form neutral alkali and ammonium salts.

3:3-Diamino-4:4′-dihydroxyarsenobenzene is suspended in water (3 parts), gently warmed with 40% formaldehyde solution (0·3 part) and 1 part of sodium hydrogen sulphite solution (40%), and the product isolated by the addition of hydrochloric acid; the free ω-*methyl-acid* is a yellowish-red powder, soluble in sodium carbonate, and decomposing when heated without fusion; the *sodium* salt is a reddish-brown mass precipitable by alcohol. F. M. G. M.